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Low-temperature microbial and direct conversion of lignocellulosic biomass to electricity: Advances and challenges

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ABSTRACT

Conversion of lignocellulosic biomass to electricity using fuel cell technologies is a promising but challenging research topic for sustainable electricity production. This is because that lignocellulosic biomass generally cannot be directly used as a fuel for electricity generation in a conventional fuel cell with high efficiency. Typical fuel cells that can convert lignocellulosic biomass to electricity under mild conditions (< 100 °C) include microbial fuel cells (MFC) and novel direct biomass fuel cells (DBFC) such as that mediated by polyoxometalates (POMs) developed recently. However, the efficiency and power output for these low-temperature fuel cells still need to be improved for practical applications. In this review, we focus on the research advances of electricity generation in fuel cells that can be operated at low temperatures. More specifically, we discussed the progress, challenge and perspectives of biomass-fueled MFCs. Recent interesting researches on DBFC were also highlighted in terms of the efficiency, principles, and technological obstacles. As concluded in this work, lignocellulosic biomass is a promising feedstock for fuel cells because it is renewable, carbon neutral, and sustainable. However, the power density of lignocelluose-fueled MFC are usually far below that required for commercial applications. Improving fermentable sugar release from lignocellulosic biomass and increasing the cell output power are the main research points. DBFC can obtain a high theoretical exergy recovery; however, it is still in its early stage of development with low efficiency. More research should be focused on the electrode development, cell design, parameter optimization, process integration, as well as understanding fundamental process mechanisms.

1. Introduction

Electricity is one of the essential forms of energy that dictates quality of life in modern society. Demand for electricity continues to grow as a result of the increase in global population and development of third-world nations [1]. In early days, electricity was generated using hydro power at remote dams or fossil fuels through combustion to drive turbines [2]. Fossil fuels are still the major energy source for electricity production. Approximately 66% of electricity is produced from fossil fuels, including 33% from coal and 33% from natural gas in 2015 in the United States (US Energy Information Administration, http://www.eia.gov/tools/faqs/faq.cfm?id=427 & t=3, last accessed July 20, 2016). However, conventional fossil-fuel-driven power plants are facing increased challenges due to emissions of pollutants and greenhouse gases. Thus, sustainable and environmentally friendly pathways for alternative electricity production using renewable resources must be developed.

Lignocellulosic biomass is a renewable natural resource that can be sustainably produced in large quantities in many regions around the world. The United States alone has the potential of sustainably producing 1.3 billion dry tonnes of lignocellulosic biomass annually from forest and agricultural lands [3]. This is equivalent to 2 trillion kWh of electricity (assuming 30% conversion efficiency from thermal energy to electricity), which is approximately 50% of the total U.S. electricity production in 2014. Electricity generation from lignocellulosic biomass has already been in commercial practice using combustion or gasification together with a steam or gas turbine (Fig. 1). However, distributed operation at relatively small scale is preferred due to the low energy density of lignocelluloses.

Fuel cell technology attracted great interest in recent years for

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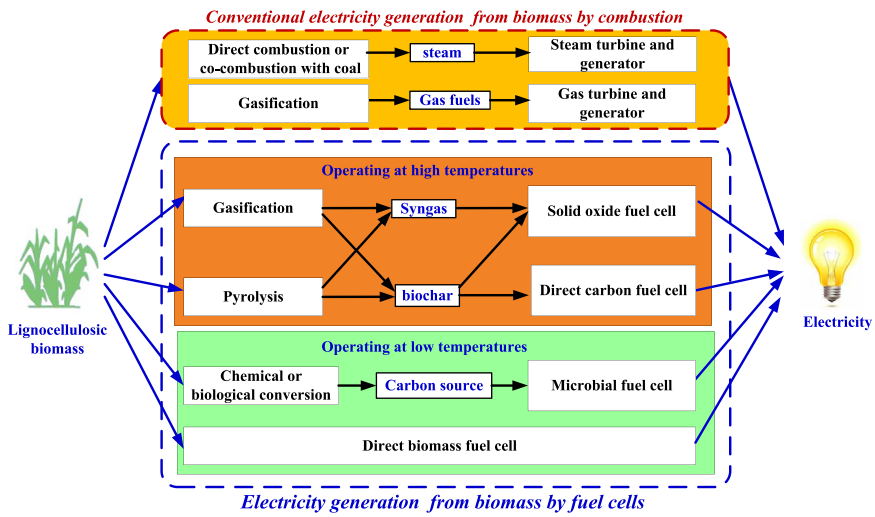

Fig. 1. Different pathways for electricity production from lignocellulosic biomass.

clean, portable, alternative electricity production and is suitable for a variety of applications. Lignocellulosic biomass-energized fuel cells can be classified into two major groups: indirect biomass fuel cells (IDBFC) and direct biomass fuel cells (DBFC). IDBFC, which has been intensively studied in recent years, refers to fuel cell technology that requires pre-converting biomass to usable fuels such as sugars (e.g., glucose and xylose), syngas, biogas, or biochar, for subsequent electricity generation in fuel cells [4]. IDBFC included solid oxide fuel cells (SOFC) and direct carbon fuel cells (DCFC) which are operated at high temperatures, as well as microbial fuel cells (MFC) operated at low temperatures. DBFC is a new technology that can produce electricity using biomass directly as fuel without preconverting or processing. DBFC technology is new with only limited research being carried out [5–8]. Low temperature fuel cells offer many advantages for many distributed applications, in this review we, therefore, focus on electricity generation from biomass via MFC and DBFC operated under mild conditions. The aim of this work is to present some basic principles, technological challenges, and future developments of these technologies.

2. Overview of lignocellulosic biomass and low temperature biomass fuel cells

Lignocellulosic biomass generally can be divided into two categories: woody biomass (including forest harvest residues and dedicated short-rotation woody crops) and herbaceous biomass (including agriculture residues such as straw and corn stover and energy crops such as switchgrass). Lignocellulosic biomass is renewable, carbon neutral in terms of reduction of CO_2 emission, and sustainable [9]. The major elemental compositions of lignocelluloses are C, H, O, N, P, and S. The elements C, H, and O mainly come from the three major components of lignocelluloses (cellulose, hemicelluloses, and lignin); N, P, and S mainly come from the minor component, such as protein. Dry lignocelluloses commonly have a C content of approximate 50%, lower than that of coal (75–90%) , and an O content of about 45%, higher than that of coal (< 20%). Lignocellulosic biomass has much higher ratios of H/C and O/C than those of fossil fuels. Thus, the heating value of lignocellulosic biomass is lower. For example, bituminous coal generally has a higher heating value (HHV) of 26 MJ kg^{-1}, while the HHV of lignocelluloses biomass is usually less than 20 MJ kg^{-1} [10,11]. Moreover, lignocellulosic biomass usually has high moisture content. Freshly cut wood typically contains 50% water by weight [12].

Lignocellulosic biomass is a complex natural material comprising three major components—cellulose, hemicelluloses, and lignin—and some minor components, such as extractives, protein, and ash. The major components account for more than 80% of the total dry weight of lignocelluloses [13,14]. However, different species of plants significantly differ in the proportions of the major components [15]. Even different parts of the same plant have different proportions of the major components. Woody biomass contains more cellulose and lignin, whereas herbaceous biomass has higher contents of hemicelluloses (mainly xylan), extractives, and ash. Generally, woody biomass contains 40–50% cellulose, 15–20% hemicelluloses, 20–35% lignin, and 0.2–1.1% ash, whereas herbaceous biomass contains 20–40% cellulose, 20–40% hemicellulose, 10–20% lignin, and 2–17% ash. Cellulose is a polysaccharide consisting of a linear chain of several hundred to more than 10,000 β (1→4) linked D-glucose units. Hemicelluloses are heteropolymers of several monosaccharide groups and uronic acid groups, including hexoses such as D-glucose, D-galactose, and D-mannose; pentoses such as D-xylose and L-arabinose; uronic acids such as D-glucuronic acid, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid; and to a lesser extent, L-rhamnose, L-fucose, and various O-methylated neutral sugars [16]. Lignin is an aromatic polymer composed of three basic monomeric units: *p*-hydroxyphenyls (H), guaicyls (G), and syringyls (S), which vary between species and cell tissue type [17]. Lignin has higher carbon content than cellulose and hemicelluloses, thus higher heating value. More details on the structures of cellulose, hemicelluloses, and lignin can be found in literatures [16,18,19].

In the three types of IDBFC (Fig. 1): microbial fuel cells (MFC), solid oxide fuel cells (SOFC), and direct carbon fuel cells (DCFC), only MFC can be operated at low temperatures. MFC use cellulose-degrading organisms with the addition of exogenous cellulase enzymes to produce electricity [20–23]. Lignocellulosic biomass need to be hydrolyzed to sugars to achieve high efficiency by microorganisms. The diversity of microorganisms in MFCs makes it possible to achieve near complete utilization of all biomass components, including lignin. DBFC can produce electricity from lignocelluloses directly with less exergy destruction because no external processing is required. Due to the complex structure of lignocelluloses and lack of efficient catalysts to effectively oxidize C-C bonds, DBFC may produce low power output. Research on DBFC is still in its early stage and this type of fuel cell shows great promising.

The performance of a fuel cell is usually characterized by several output parameters, such as open circuit voltage (OCV), current density (CD), power density (PD), and coulombic efficiency (CE). These terms are defined as follows: open circuit voltage is the maximum voltage available from a fuel cell at zero current in V or mV; current density is the current per unit area of electrochemical-active electrode (anode) in mA cm^{-2}; power density is power output per unit area or volume in mW cm^{-2} (or W cm^{-2}) coulombic efficiency, also called Faradic effi-

ciency. It is the percentage of total produced coulombs to the theoretical amount of coulombs available from the fuel. The cell efficiency will be discussed regarding to these parameters.

3. Microbial fuel cells (MFC)

3.1. Principles of MFC

MFC as a bio-electrochemical system convert bio-convertible chemical compounds to electricity under the catalytic activity of micro-organisms [24]. The concept of MFC can be traced back to as early as 1911 when Potter found that decomposition of organic compounds by micro-organisms was accompanied by liberation of electrical energy [25]. However, not until the 1980s did MFC attract attention for treating wastewater. With improved power output, MFC became promising for practical applications in the past decade [26]. The basic principles of a lignocellulosic biomass-fueled dual-chamber MFC are shown in Fig. 2. Biomass is first converted to substrate fuels such as glucose, xylose, acetate, which are utilized as carbon sources by micro-organisms. The MFC consists of an anode, a cathode, a proton or cation exchange membrane (PEM or AEM), and an external electrical circuit. In the anode chamber, the micro-organisms convert the fuels into CO_2, protons, and electrons. The electrons are transferred to an insoluble electron acceptor, the anode, via redox mediators and then flow through an electrical circuit with a load to the cathode. Electrical power thus is generated by the potential difference between the anode and cathode. In the anode chamber, the protons flow through PEM to the cathode, where they combine with oxygen and electrons to form water [27]. The micro-organism is the "bridge" linking between chemical energy of the substrate compounds and electric energy.

Various micro-organisms have been used in MFC as listed in Table 1. They obtain energy to support their life by transferring electrons produced from the oxidation of organic compounds to metabolic products and finally to CO_2 in a MFC [28]. Thermodynamically, this energy comes from the change of free energy (ΔG_{ox}) for the oxidation of the substrates by exogenous oxidants. Respiration and fermentation are two identified major metabolic pathways for electron transfer [28]. However, the mechanism of anodic electron transfer has not been clearly understood and identified. Electron transfer between a microbe and an electrode can be possibly mediated by (a) a direct connection of the active center of the cell membrane enzyme to the electrode; (b) biological nanowires of 2–3 mm long called *pili*, made of fibrous protein structures; or (c) added or naturally occurring redox active species that are stable in two redox states and able to quickly diffuse in and out of the enzymatic channels, hence effectively shuttling electrons from the enzyme active site to the electrode surface [29]. We are not going to analyze this issue in depth in this review. Interested readers are referred to published studies instead [26,28–32].

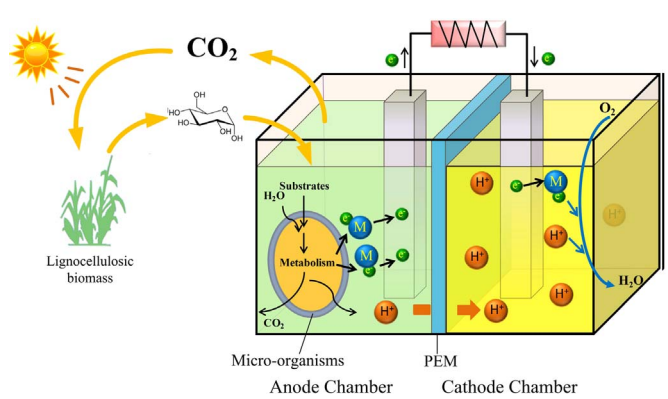

Fig. 2. Principles of lignocellulosic biomass fueled dual-chamber MFC with addition of electron mediator.

3.2. Biomass-derived substrate fuels for MFC

Many organic compounds, such as cellulose [33], cattle manure [34,35], pretreated corn stover [20] and marine algae [36], can be directly used in MFC for electricity generation. However, many micro-organisms are not capable of efficiently hydrolyzing cellulose anaerobically and electrochemically active to use anode as an electron acceptor, which results in a low MFC power density [37]. For example, when 1 g L^{-1} rice straw was used directly as fuel, Gurung and Oh found that the maximum power density was only 0.019 mW cm^{-2} [38]. Using a novel three-chamber MFC, Krishnaraj et al. achieved a maximum power output of 8.78 W m^{-3} at 20.95 A m^{-3} and 6.73 W m^{-3} at 17.28 A m^{-3} with sugarcane bagasse and corn cob as substrates, respectively. However, these output powers are too low to be meaningful for commercial applications [39]. To improve MFC efficiency, a pre-hydrolysis step is often used to obtain monosaccharides or other fermentable compounds, such as degraded phenolic compounds, organic acids including acetic acid from hydrolysis of acetyl groups, and furan derivatives such as furfural and 5-hydroymethylfurfural (HMF) from sugar degradation (Table 1). Pre-hydrolysis always simultaneously produces various types of fermentable compounds for MFC.

Sugars, especially glucose, are the most important biomass-derived fuels for MFC. Most micro-organisms have developed mature metabolic system to utilize glucose for energy production. Stoichiometrically, 24 electrons are released by complete oxidization of each molecule of glucose (Table 2). PD of glucose-fueled MFC ranges from thousandth to a fraction of mW cm^{-2} (Table 1) depending on the micro-organisms, culture conditions, fuel cell designs, operation models (batch, fed-batch, or continuous), terminal oxidizing agents, and other factors. However, glucose is an easily fermentable substrate that can be consumed by many competing metabolisms, such as fermentation and methanogenesis. These metabolic pathways do not produce electricity and thus can reduce CE [40].

Hydrolysis of hemicelluloses produces a variety of sugars (including hexose and pentose), uronic acids, and acetic acid. These organic compounds can also be promising carbon sources for MFC. The maximum PD from several monosaccharide carbon sources, i.e., six hexoses, three pentoses, two uronic acids, and one aldonic acid (Table 1), ranged from 0.1240 to 0.277 mW cm^{-2}, with a CD range of 0.76–1.18 mA cm^{-2} and a CE range of 21–37%. D-mannose produced the lowest maximum PD and D-glucuronic acid the highest (Fig. 3) [41]. The PD generated by these biomass-derived monosaccharides is greatly dependent on the metabolic ability of the bacteria in using these compounds. Micro-organisms often need time to adapt to a new carbon source. Very long adaptation time is required for mixed bacteria to use arabinose compared with glucose [41]. Xylose is the most abundant pentose contained in hydrolysates of herbaceous biomass and hardwoods. Fortunately, most MFC bacteria can easily utilize xylose as a carbon source. PD reached 0.233 mW cm^{-2} with a CE of 31% when using pure xylose, even higher than using glucose [41]. CE could be enhanced to 54% by adopting continuous operation with a hydraulic retention time of 38 h [42]. Uronic acids are usually found in dilute acid hydrolysates of lignocelluloses; however, little work on uronic acids as carbon sources for MFC were carried out. On the other hand, D-glucuronic acid produced higher power density than sugars [41].

Phenolic compounds from lignin degradation are considered as inhibitors to micro-organisms [43], but these compounds can be used for MFC because some bacteria are capable of degrading phenol. The constituent of phenolic compounds differs depending on lignin structure. Typical phenolic compounds in acid hydrolysates of lignocelluloses are vanillin, syringaldehyde, catechol, 4-hydroxybenzoic acid, and their derivatives [43,44]. Few works mentioned the potential of these compounds as fuels for MFC. A single-chamber MFC produced a current of 178 μA using veratryl alcohol (VA) at 500 mg L^{-1} in fed-batch mode [45]. PD could be significantly increased when using a

Table 1
Some reported works on MFCs using substrates that can be potentially derived from lignocellulosic biomass.

Substrate	Substrate can be from	Micro-organisms	Electrode	Oxidizing agent	Power density (mW cm^{-2})	Reference
Glucose	Hydrolysis of cellulose	Anaerobic sludge	Carbon felt (anode) and carbon cloth with Pt (cathode)	Air (oxygen)	0.00313	[153]
		Bacteria present in wastewater	Carbon paper (anode) and carbon paper coated with Pt (cathode)	Air (oxygen)	0.0262 (with PEM) 0.0494 (no PEM)	[154]
		Shewanella sp. HN–41	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen) and $K_3Fe(CN)_6$	0.00182	[73]
		Saccharomyces cerevisiae	Graphite felt	$K_3Fe(CN)_6$	0.0065	[93]
		Saccharomyces cerevisiae	Graphite felt	$KMnO_4$	0.0234	[93]
		Pre-domesticated bacteria for MFC	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.1488	[48]
		mixed microbial consortium	Graphite felt cut into circular discs	Air (oxygen)	0.138	[36]
		Saccharomyces cerevisiae	Carbon rods and carbon fiber bundles	$K_3Fe(CN)_6$	0.0022	[155]
		Kluyveromyces marxianus	Carbon rods and carbon fiber bundles	$K_3Fe(CN)_6$	0.0022	[155]
		Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.216	[41]
		Bacteria present in wastewater	Carbon paper	Air (oxygen)	0.0028	[156]
Mannose	Hydrolysis of hemicellulose	Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.124	[41]
Galactose	Hydrolysis of hemicellulose	Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.209	[41]
		Proteus vulgaris	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Ferricyanide	N.A (56% coulombic efficiency)	[157]
Xylose	Hydrolysis of hemicellulose	Pre-domesticated bacteria for MFC	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.1406	[48]
		Kluyveromyces marxianus	Carbon rods and carbon fiber bundles	$K_3Fe(CN)_6$	0.00112	[155]
		Mixed bacteria	Graphite fiber brushes (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.0673	[42]
		Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.233	[41]
		Xylose dehydrogenase surface displayed bacteria	Modified glassy carbon	Oxygen	0.063	[158]
		Bacteria present in wastewater	Carbon paper	Ari and potassium hexacyanoferrate	0.00063	[159]
		Bacteria present in wastewater	Carbon paper	Air (oxygen)	0.0032	[156]
Arabinose	Hydrolysis of hemicellulose	Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.203	[41]
Rhamnose	Hydrolysis of hemicellulose	Pre-domesticated bacteria for MFC	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.0014	[48]
		Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.132	[41]
Glucuronic acid	Hydrolysis of hemicellulose	Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.277	[41]
Gluconic acid	Hydrolysis of hemicellulose	Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.205	[41]
Galacturonic acid	Hydrolysis of hemicellulose	Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.148	[41]

(continued on next page)

Table 1 *(continued)*

Substrate	Substrate can be from	Micro-organisms	Electrode	Oxidizing agent	Power density (mW cm^{-2})	Reference
Acetate	Hydrolysis of acetyl group in hemicellulose or bioconversion from biomass sugars	Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.112 (fed-batch)	[160]
		Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.18 (continuous)	[160]
		Geobacteraceae-enriched culture	Glass chips coated with Ti/Au	$K_3Fe(CN)_6$	0.0047	[161]
		Geobacter sulfurreducens	Carbon cloth	$K_3Fe(CN)_6$	0.188	[162]
		Bacteria present in wastewater	Carbon paper	Air (oxygen)	0.0123	[156]
Phenolic compounds (phenols, veratryl alcohol, vanilin etc)	Degradation of lignin	Anaerobic sludge	Carbon felt (anode) and carbon cloth with Pt (cathode)	Air (oxygen)	0.00165	[153]
		Mixed aerobic activated sludge and anaerobic sludge	Carbon paper (anode) and carbon paper coated with Pt (cathode)	Air (oxygen)	0.0006	[163]
		Aerobic and anaerobic activated sludges	Graphite fiber brushes	$K_3Fe(CN)_6$	35.17 (W/ m^3)	[45]
		Anaerobic sludge	Carbon felt (anode) and carbon cloth with Pt (cathode)	Air (oxygen)	0.00313	[153]
Mixed sugars	Hydrolysis of biomass	Mixed bacteria	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.0602	[164]
Furan derivatives	Degradation of sugars	Anaerobic and aerobic sludge	carbon fiber brush	Ferricyanide	0.0361	[47]
Biomass hydrolysate	Hydrolysis of biomass	Pre-domesticated bacteria for MFC	Carbon cloth (anode) and carbon cloth coated with Pt (cathode)	Air (oxygen)	0.1027	[48]
		Bacteria present in wastewater	Carbon paper (anode) and carbon paper coated with Pt (cathode)	Air (oxygen)	0.0367	[49]
		Bacteria present in wastewater	Carbon paper (anode) and carbon paper with diffusion layer coated with Pt (cathode)	Air (oxygen)	0.0971	[49]
		Bacteria present in wastewater	Carbon paper	Air (oxygen) and $K_3Fe(CN)_6$	0.0148	[51]
		Bacteria present in wastewater	Carbon paper	$K_3Fe(CN)_6$	0.0123	[50]
Biorefinery wastewater	Biomass pretreatment	Bacteria consortium	Carbon felt (anode) and carbon felt coated with Pt (cathode)	Air (oxygen)	0.118	[165]
		Exoelectrogenic microbial consortium	Carbon felt (anode) and carbon felt coated with Pt (cathode)	Air (oxygen)	0.37	[113]

Table 2
Theoretical anodic half cell and overall oxidation reactions for different biomass-derived substrates used in MFCs.

Substrates	Theoretical anodic half cell reaction and overall reaction	Electron released (mol kg^{-1} substrate)	Standard ΔG for overall reaction (kJ kg^{-1} substrate)
Hexoses	$C_6H_{12}O_6+6H_2O \rightarrow 6CO_2+24H^+ +24e^-$	133.3	
Glucose	$C_6H_{12}O_6+6O_2 \rightarrow 6CO_2\uparrow + 6H_2O(l)$		−15699.60[a]
Galactose			−15652.98[a]
Mannose			−15696.33[b]
Pentoses	$C_5H_{10}O_5+5H_2O \rightarrow 5CO_2+20H^+ +20e^-$	133.3	
Xylose	$C_5H_{10}O_5+5O_2 \rightarrow 5CO_2\uparrow + 5H_2O(l)$		−15754.41[b]
Arabinose			−15809.43[b]
Uronic acids			
Glucuronic acid	$C_6H_{10}O_7+5H_2O \rightarrow 6CO_2+20H^+ +20e^-$	103.1	
Galacturonic acid	$C_6H_{10}O_7 + 5O_2 \rightarrow 6CO_2 \uparrow +5H_2O(l)$	103.1	
Acetic acid	$CH_3COOH + 2H_2O \rightarrow 2CO_2 +8H^+ +8e^-$	133.3	
	$CH_3COOH + 2O_2 \rightarrow 2CO_2 \uparrow + 2H_2O(l)$		−14150.08[a]
Lactic acid	$C_3H_6O_3+3H_2O \rightarrow 3CO_2 +12H^+ +12e^-$	133.3	
	$C_3H_6O_3+3O_2 \rightarrow 3CO_2 \uparrow +3H_2O(l)$		−15000.22[a]
Phenol	$C_6H_6O+11H_2O \rightarrow 6CO_2 +28H^+ +28e^-$	297.9	
	$C_6H_6O + 7O_2 \rightarrow 6CO_2\uparrow + 3H_2O(l)$		−31633.41[a]
Vanillin	$C_8H_8O_3+13H_2O \rightarrow 8CO_2 +34H^+ +34e^-$	223.7	
	$C_8H_8O_3 + 17/2O_2 \rightarrow 8CO_2 \uparrow +4H_2O(l)$		
Furfural	$C_5H_4O_2+8H_2O \rightarrow 5CO_2 +20H^+ +20e^-$	208.3	
	$C_5H_4O_2+5O_2 \rightarrow 5CO_2\uparrow + 2H_2O(l)$		−22332.64[c]

[a] calculated with the standard Gibbs free energy of formation from Lange's Handbook of Chemistry [166];
[b] calculated with the standard Gibbs free energy of formation from ref. [167];
[c] calculated with the standard Gibbs free energy of formation from ref. [168].

mixture of glucose and VA. Lignin can also be used as electron mediator to improve PD [46] because the benzene ring has abundant electron distributions.

Other by-products from hydrolysis of lignocelluloses were also promising carbon sources for MFC. Acetate (acetic acid) produced from hydrolysis of acetyl group on hemicellulose backbone is an ideal substrate for MFC because acetate can be easily assimilated by electroactive bacteria. An acetate-fed MFC showed a high CE (72.3%), much higher than those of butyrate (43.0%), propionate (36.0%), and glucose (15.0%) [40]. Furfural, another acid hydrolysis by-product, was used as the sole fuel in both the ferricyanide-cathode and the air-cathode MFC. A PD of 0.0361 mW cm^{-2} and CE of 30.3% were obtained in an air-cathode MFC using 6.68 mM furfural. Increasing furfural concentration resulted in somewhat increased maximum PD [47].

Biomass hydrolysates are mixtures of sugars, phenolic compounds, organic acids, and sugar derivatives, all have been directly used in MFC [48–51]. Reported PD ranged from 0.01 to more than 0.1 mW cm^{-2} (Table 1), with CE ranging from 15–40%, depending on MFC types and the micro-organisms used. PD achieved using a hydrolysate from *Enteromorpha prolifera*, an algae biomass [48], and a steam-exploded corn stover hydrolysate [49] were similar to those achieved using monosaccharides. A higher PD was also reported using a biomass hydrolysate than using only xylan or carboxylic acids [51], perhaps due to the presence of phenolic compounds that mediate electron transport. Nevertheless, degradation products such as furan derivatives and phenolic compounds present in hydrolysates are usually inhibitive to micro-organisms, particularly to pure culture [52]. This has become one obstacle to the development of biomass-energized MFC, as will be discussed later.

3.3. Factors affecting performance of MFC

3.3.1. Microorganism, substrate fuels, and operation conditions

Although some yeasts, such as *Saccharomyces cerevisiae* [53,54], *Arxula adeninivorans* [55] and *Candida melibiosica* [56,57], have been employed as catalysts in MFC, electricity-generating bacteria, such as *Actinobacillus succinogenes* [58], *Clostridium* species [59,60], *Escherichia coli* [61–63], *Geobacter* species [64–66], *Klebsiella pneumoniae* [67,68], *Pseudomonas* species [69,70], and *Shewanella* species [71–73], are commonly used. Both pure culture and mixed bacterial communities have been attempted (Table 1). Mixed bacterial communities often produced much higher PD and consumed more biomass hydrolysate than pure culture because pure culture is incapable of metabolizing a diverse of compounds in hydrolysates. For example, *Geobacter* species primarily can use only organic acids, ethanol, and aromatic compounds [74]; *Pseudomonas* can use only glucose but cannot utilize fermentative products such as acetate [75]; *Shewanella* species can only partially oxidize a limited number of organic acids, such as lactate, pyruvate, and acetate under anaerobic conditions [74]; *Enterobacter* sp. primarily use glucose [76]; and *Saccharomyces cerevisiae* showed very low utilization of pentose such as xylose [77,78]. In using mixtures of microbial consortium, electrons are transferred from substrates to electrode via an electron transport system that consists of a series of components in the bacterial extracellular matrix or together with electron shuttles in the bulk solution [41]. Bacteria in the consortium played different roles in consuming hydrolysate as found in a two-chamber MFC using a hydrothermal hydrolysate of wheat straw [50]. The consortium mainly consisted of *Bacteroidetes* (40%), *Alphaproteobacteria* (20%), *Bacillus* (20%), *Deltaproteobacteria* (10%), and *Gammaproteobacteria* (10%), while the suspended consortia were predominately *Bacillus* (22.2%). The microbial community composition may change after MFC operation depending on niches, sulfate-reducing bacteria accounted for large relative abundance [79].

Substrate fuel is an important factor for power generation in MFC. Various biomass-derived compounds have been used. Theoretical anodic half-cell reactions and standard changes in Gibbs free energy for different biomass-derived substrates are shown in Table 2. Phenolic compounds and furfural theoretically can provide more electrons and higher Gibbs free energy changes than carbohydrates under complete oxidation. However, the practical PD for a giving substrate is greatly

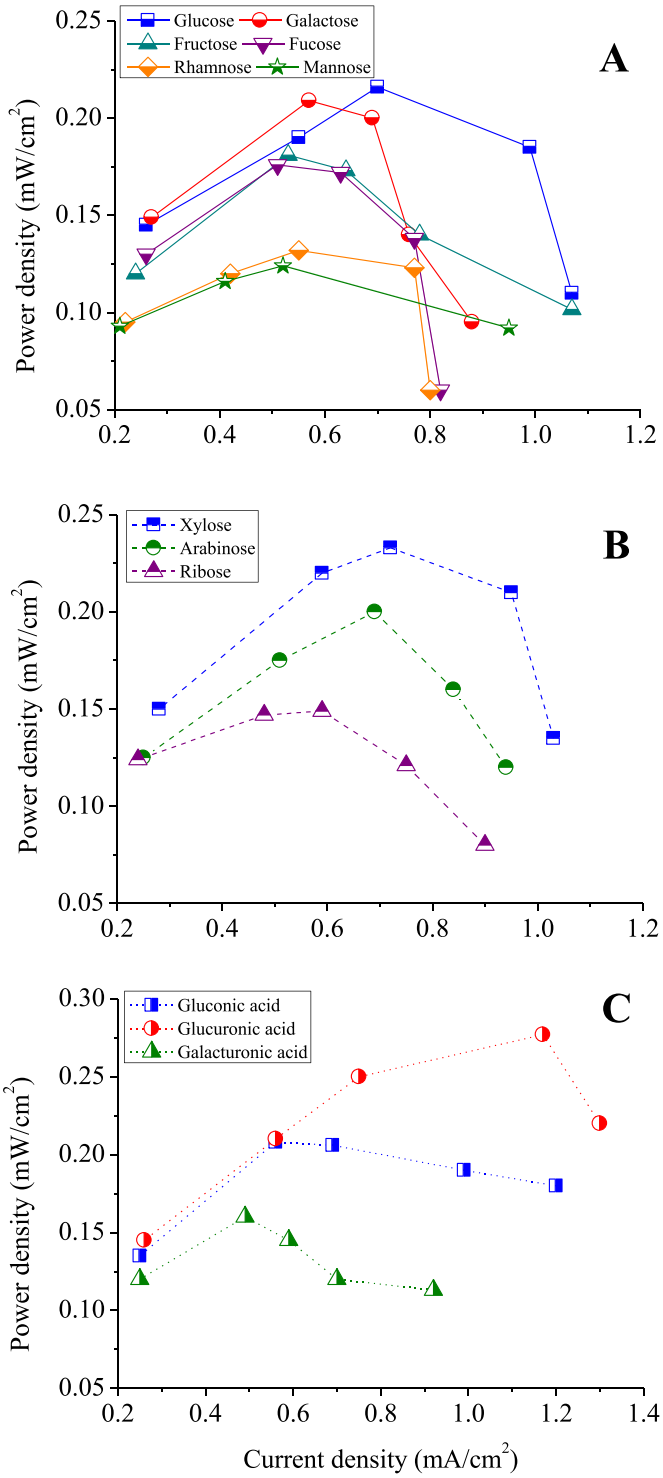

Fig. 3. Power densities as a function of current density in MFC using different carbon sources that can be derived from lignocellulosic biomass. A: hexoses; B: Pentoses; C: uronic acids (Redrawn after [41]).

dependent on its "digestibility" by the micro-organisms. The bacteria indeed showed preference in using carbon sources. Generally speaking, acetate is the most preferred substrate with relatively high CE [37]. Sugars are also good substrates. Hexoses are usually more preferentially used by bacteria with higher utilization rates than pentoses [80]. Sugar degradation products and phenolic compounds are more difficult to use and toxic to micro-organisms, as will be discussed later. For utilizing phenol and phenolic derivatives, the micro-organisms have to secrete enzymes such as monooxygenases that can decompose aromatic toxic compounds [81]. The substrate concentration also shows important influence. The maximum power obtained at different initial substrate concentrations often can be fit to a Monod-type curve [49].

pH is an important factor influencing MFC power generation [82–85]. pH changes in anodic and cathodic chambers are negligible when consumption rate of protons at the cathode equals production rate at the anode. However, pH is often reduced (increased proton concentration) in anode chamber while increased in cathode chamber. Controlling pH shifts at the cathode and anode by using a phosphate buffer (pH 7.0) can increase current output by 100–200% [86]. Optimal pH for producing maximum power was 8–10 in an air-cathode MFC fueled with acetate. Furthermore, the anodic microbial process preferred a neutral pH, whereas the cathodic reaction was improved at a weak alkaline pH [82]. Therefore, using a buffer can improve the efficiency of MFCs because it can stabilize pH to facilitate microbial metabolic activities as well as compensate for the slow proton transport rate to improve cathodic reaction [27].

Other operational factors such as operation mode (batch, fed-batch, continuous flow) [87], temperature [88–90], and startup cultivation can also influence the performance of pure sugar-fueled MFC. However, limited studies were carried out on the biomass hydrolysate-fueled MFC.

3.3.2. Final electron acceptor

In most MFC, oxygen (air) is used as the final electron acceptor for the cathodic reaction (air-cathode) (Table 1). Thus the power output of an air-cathode MFC strongly depends on the level of dissolved oxygen (DO). DO supply was a limiting factor to cathode reaction in a mediator-less MFC with external resistance lower than 500 Ω due to the limitation in oxygen mass transfer [86]. Using a dissolvable electron acceptor such as ferricyanide can improve electricity output. Maximum power output was increased by 50–80% when using ferricyanide instead of dissolved oxygen [91]. The reported PD reached as high as 0.72 mW cm^{-2}, compared with less than 0.1 mW cm^{-2} using DO [27], perhaps due to the greater mass transfer of ferricyanide and lower activation energy for the cathodic reaction [91]. Other electron acceptors such as H_2O_2 [92] and potassium permanganate [93] also have been used. PD was greatly improved using H_2O_2 in a two-compartment continuous-flow MFC compared with that using aeration (oxygen) [92]. Even higher PD was produced using potassium permanganate as an electron acceptor than that using potassium ferricyanide [93]. However, these "powerful" electron acceptors are often much more expensive than oxygen.

3.3.3. Electrode materials

The materials of electrodes affect the performance and cost of MFC. The most commonly used materials for anodes are carbon-based, such as granular activated carbon, graphite rod, graphite fiber brush, carbon paper, cloth, felt, and reticulated vitreous carbon (RVC). Each of these electrodes has its own advantages and disadvantages [94]. The anode materials should possess not only good electron conductivity, but also high availability for bacteria attachment. The surface properties of an anode, such as roughness, porosity, and surface wettability, influence the formation of biofilm and subsequent power output. The amount of bacteria attached is proportional to the surface porosity of carbon papers [95]. Materials with hydrophilic surfaces are more suitable for anodes. The commonly used carbon materials have limited surface areas for biofilm growth and subsequent electron transfer [96]. In recent years, nano-composite materials, such as nano-structured carbon, nanofibers, and nanotubes, have attracted great interest as electrode materials because they are more conductive and mechanically stable with larger surface area and higher electrochemical catalytic activity compared with the conventional carbon electrodes [97]. When using activated carbon nanofibers (ACNFs) as anode instead of carbon, higher power output with higher substrate utilization efficiency was obtained [96]. However, these nano-structured carbon electrodes were

found toxic to the microbial consortium in the biofilm, which reduces the long-term performance of MFC [97].

For an air-cathode, Pt-coated carbon materials are usually used (Table 1). The Pt deposited on an air-cathode can improve power output by increasing the affinity to oxygen and decreasing the activation energy of the cathodic reaction [98]. Modification of the cathode with metal ions such as Fe(III) and/or Mn(IV) can also greatly improve electricity generation [99,100]. Modifying the cathode with the addition of a diffusion layer to increase cathode surface area can improve electricity generation because diffusion of oxygen in the electrode is important. The maximum power produced from a single-chamber MFC using neutral or acid hydrolysates of corn stover can be increased by more than 100% by adding a diffusion layer to the cathode [49].

A statistical analysis using PCA/UMR approach was conducted for a *Shewanella oneidensis* MFC to discern the relative importance of various factor on MFC performance [101]. Buffer pH is a main parameter determining MFC performance. Reducing carbon source concentration has a positive effect. Electrode area and compartment volume have the highest effect on maximum power. Analyte content and anode material mostly affect the maximum current.

3.4. Obstacles in using lignocellulosic biomass for MFC

3.4.1. Biomass recalcitrance for sugar release

There are generally two ways to release sugars from lignocellulosic biomass, namely acid hydrolysis and enzymatic hydrolysis. However, the recalcitrance of lignocelluloses is the main obstacle that prevents efficient release of sugars, especially glucose, from biomass to energize MFC due to its hierarchical structure that resists the attack of chemicals or enzymes to its structural polysaccharides [102]. The hemicelluloses and lignin strengthen the cell wall. Crystalline cellulose is highly ordered due to the hydrogen bond network and is very stable and difficult to be permeated even by water molecules [103]. Moreover, anatomically plant cell wall is largely honeycomb-like and composed of distinct layers. This multilayered structure acts as a natural barrier to further prevent chemicals and enzymes from permeating into the wall [18]. Therefore, severe conditions (high temperature or acid concentration) must be employed [104], which results in substantial sugar degradation. Efficient enzymatic hydrolysis of lignocelluloses requires pretreating biomass to increase cellulose accessibility. Unfortunately, pretreatments are usually energy intensive with high cost. Interested readers are referred to published papers on biomass recalcitrance [13,105] and biomass pretreatments [14,106–110].

3.4.2. Inhibition by inhibitors present in the hydrolysate

Another obstacle for using lignocellulosic biomass hydrolysate in MFC is the inhibition of micro-organisms by toxicants. This inhibition is more problematic for pure culture than for a bacterial consortium. Theses toxicants are formed during the process of producing biomass hydrolysate via degradation reactions of hydrolysis products. They include sugar degradation products such as furans (furfural, 5-HMF) and organic acids (including acetic acid, formic acid, and levulinic acid), and phenolic compounds from lignin degradation. The mechanisms of these compounds inhibit fermentation performance of yeast such as *Saccharomyces cerevisiae* and bacteria such as *Escherichia coli* have been intensively studied [43,111,112]. However, their inhibition on MFC performance have not been well investigated. Most of these by-products can be utilized as substrate fuels when glucose is used up. Mixed bacteria such as active sludge or screen bacterial consortium are required to obtain efficient power output. HMF, trans-cinnamic acid, and 3,5-dimethoxy-4-hydroxycinnamic acid at concentrations up to 10 mM did not affect MFC electricity generation using glucose. Syringaldeyhde, vanillin, trans-4-hydroxy-3-methoxy, and 4-hydroxy cinnamic acids inhibited electricity generation at concentrations above 5 mM, whereas 2-furaldehyde, benzyl alcohol and acetophenone at concentrations less than 0.2 mM (Fig. 4) [52]. On

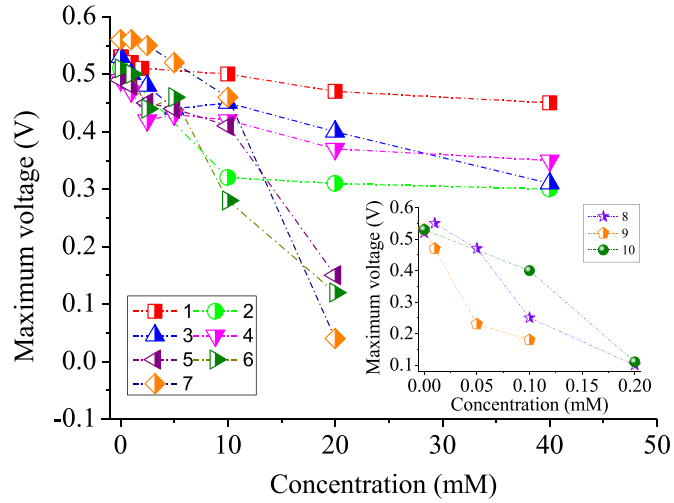

Fig. 4. Effects of furan derivatives and phenolic compounds on electricity generation in MFC with glucose as a carbon source. 1: 5-HMF; 2: vanillin; 3: trans-cinnamic acid; 4: 3,5-dimethoxy-4-hydroxy cinnamic acid; 5: syringaldeyhde; 6: trans-4-hydroxy-3-methoxy cinnamic acid; 7: 4-hydroxy cinnamic acid; 8: furaldehyde; 8: acetophenone; 10: 3,4-dimethoxybenzyl alcohol (data from [52]).

the other hand, furfural did not decrease voltage output when concentration was increased from 0.1 g L^{-1} to 2 g L^{-1} (20.8 mM) [113]. Phenolic compounds might improve MFC efficiency. For example, 20% higher PD with higher CE were obtained using a wheat straw hydrolysate than those using a synthetic medium [51]. A similar phenomenon was observed when humic acid was added to a xylose-fueled two-chamber MFC [114]. This is because the aromatic ring structure of phenolic compounds can accept an extra electron and thereby facilitate the shift between oxidized and reduced states [115]. The inhibitory effects of hydrolysate by-products also depend on the bacteria consortium. More investigations of the subject are needed.

Another inhibition by hydrolysate may come from the ash of biomass and salts from hydrolysate neutralization. Lignocellulosic biomass usually has an ash content ranging from 0.2–17%, depending on species [13]. The determined metal ions contained in the biomass ashes mainly include Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, and Ti^{4+} [116]. Most of these metal ions can be dissolved in the hydrolysate during acid hydrolysis. The acid hydrolysate usually needs to be neutralized before use. A great amount of salts such as gypsum is produced. These salts may inhibit micro-organisms to affect MFC performance. High salt concentration can create high osmotic pressure and inhibit the growth of micro-organisms. Some metal ions may show negative influence on the PEM or AEM by forming inorganic salt precipitations, thus fouling PEM [117,118]. The precipitation of calcium and magnesium may cause an inorganic scaling on the surface of AEM, thus increasing the membrane resistance to hydrogen ions [119].

4. Direct biomass fuel cells (DBFC)

Direct biomass fuel cell (DBFC) refers to technologies that can directly convert polymeric natural biomass, such as trees, grasses, agricultural residue, algae, and other biological material, to electricity. At ideal conditions, the natural biomass could be directly used as the fuel in fuel cells without purification or chemical pretreatment. However, current direct biomass fuel cell technologies can use only purified biomass, such as starch or cellulose. For example, purified biomass such as starch, cellulose or lignin were dissolved under alkaline conditions and used as fuels with noble metals (e.g., Pt, Pd, or Au) as catalysts in proton exchange membrane fuel cells (PEMFCs) [120–122]. Certainly, fuel oxidation is not complete because noble metal catalysts lack the ability to efficiently oxidize large molecules

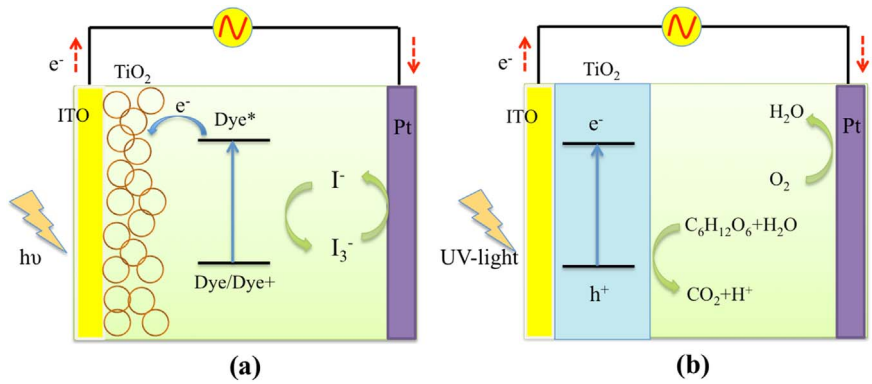

Fig. 5. Comparison of working principle of dye sensitive solar cell (DSSC) (a) and photo fuel cell (PFC) (b)(Redrawn after [138,169]).

electrochemically. For this reason, PD is substantially lower than using liquid alcohol fuels. While directly using biomass in fuel cells provides a renewable and more sustainable way for energy production, many challenges and constraints remained.

4.1. Technical difficulties of direct biomass utilization in fuel cells

Biomass is intrinsically different from small-molecular fuels, such as methanol, ethanol, or glycerol. First, lignocellulosic biomass is in the form of a solid and intrinsically insoluble in water or most organic solvents. Most biomass polymers require pretreatment and dispersal in solution to overcome mass transfer limitation of large molecules. For example, native cellulose is inactive in commercial PEM fuel cells because of the rigid crystalline structure, and it also resists enzymatic hydrolysis in MFC owing to the lack of available hydrolysis sites [123]. Second, there is a lack of efficient catalyst for polymeric biomass degradation and oxidation at low temperatures. Current noble metal catalysts (e.g., Pt, Pd, and Ru) are not able to effectively cleave C–C bonds in organic molecules at low temperatures [124,125]. PEM fuel cells have very low power output and energy efficiency [126]. As a result, the natural polymeric biomass (e.g., starch, cellulose, lignin) cannot be effectively electro-oxidized in conventional low-temperature PEM fuel cells. Finally, many contaminants in raw biomass can be poisonous to fuel cell catalysts. The noble metal catalysts show low resistivity to the impurities in biomass, even at ppm levels [127,128]. Catalytic activities can be irreversibly lost because of the poison elements or intermediate products during biomass oxidation, such as CO. Therefore, raw biomass may require a series of process purification and pretreatment steps prior to being applied in fuel cells, such as torrefaction, acid/alkaline treatment, or pyrolysis [129–132]. Polymeric biomass can be degraded to small-molecule fuels such as CH_4 or ethanol by fermentation, or converted to bio-oil or gases by pyrolysis or gasification [133–135]. Undoubtedly, the economic benefit and environmental advantages of biomass are devalued due to the pretreatments.

4.2. Photofuel cells (PFC)

A photofuel cell (PFC) is based on the mechanism of solar cells but differs because the former is powered by fuels whereas the latter solely depends on the conversion of solar energy. In solar cells, photosensitive dyes are excited by absorbing light and inject the excited electrons into conductive band of TiO_2. Then, the I^-/I_3^- redox couple plays as an electron shuttle that can accept electrons from external circuit on a counter electrode (Pt), and it can deliver the electrons to oxidized dyes in an electrolyte, leading to regeneration of the ground state dye (Fig. 5). The redox couple is abandoned in PFC so that the dissolved biomass fuels are directly oxidized by photo-excited holes on the TiO_2 anode. The excited electrons go through an external circuit and are accepted by O_2 on the cathode (Pt). Therefore, the total reaction in a PFC is the oxidation of biomass by O_2, with light irradiation.

Various polymeric biomass fuels or bio-related materials can be photo-decomposed in a PFC with an O_2-reducing cathode, such as soluble starch, carboxymethyl cellulose, lignosulfonic acid, and other soluble small organic molecules [136–139]. The fuels should be either liquid or soluble in water and are required to be highly concentrated. The biomass fuels in PFC are photo-decomposed and almost stoichiometrically oxidized to CO_2 as demonstrated by experiments using methanol, ethanol, and glucose as fuels [140]. When the cathode was replace with air, not pure O_2, it could decrease the fill factor (FF) value but still showed distinct PFC characteristics.

The output power is low in direct biomass-fueled PFC, usually less than 0.1 mW cm^{-2}. Actual open circuit voltage (V_{oc}) is about two-third or one-half of the theoretical value, or in some cases even lower. However, Kaneko *et al.* recently constructed an n-semiconductor-metal nanocomposite anode that had a Schotty-junction/ohmic contact effect in PFC [141]. This design significantly improved the performance of direct biomass PFC, with a power density of 2 mW cm^{-2}. Because the TiO_2 anode can absorb only short wavelength light (< 400 nm), the PFC performance may be improved by introducing a new photo-catalytic anode.

4.3. Liquid catalyst fuel cells (LCFC)

4.3.1. Principle of LCFC

Recently, Yulin Deng's group at Georgia Institute of Technology reported novel solar- or head-induced hybrid fuel cells that can directly consume biomass without chemical pretreatment [5]. The new biomass fuel cell employs polyoxometalates (POMs) in solution as a photo-catalyst and charge carrier to realize a new pathway for direct biomass-to-electricity conversion.

The novel direct biomass fuel cell consists of two liquid POM catalyst solutions, a liquid catalyst fuel cell (LCFC), including a common fuel cell equipped with a membrane electrode assembly (MEA) and a transparent glass fuel storage vessel that can be pre-irradiated with light (Fig. 6). The anode was fabricated with a simple carbon electrode without Pt for POM solution discharging. In contrast, the cathode can be constructed with noble metals with oxygen [5] or by carbon with a different POM solution [6]. In the cathode, biomass-POM electrolyte solution was irradiated by sunlight or heating until the color changed from yellow to deep blue, and then pumped and circulated in the anode cell.

The direct biomass-consuming LCFC can be powered by various biomass types, such as starch, cellulose, switch grass, wood powder, isolated lignin and polyols [5–8]. The power density can reach 51 mW cm^{-2} when fueled by fresh bush allamanda, similar to most methanol fuel cells (Fig. 7), and is 3,000 times higher than cellulose based MFC.

The catalysis mechanism is unique and different from a traditional PEM fuel cell. The mechanism includes three major steps (see Fig. 8):

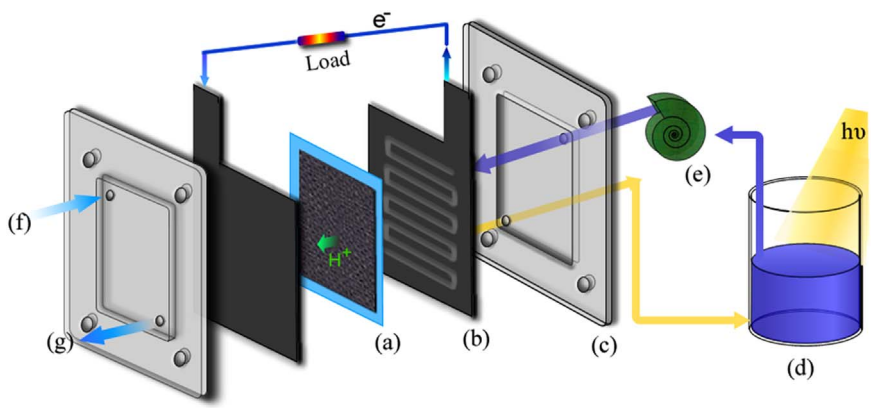

Fig. 6. Structure of the solar-induced hybrid liquid catalyst fuel cell (LCFC): (a) membrane electrode assembly (Nafion® 117 PEM, anode made of carbon cloth and cathode loaded with Pt/C catalyst), (b) graphite bipolar plate, (c) acrylic plastic end plate, (d) transparent glass vessel with PMo_{12}-starch solution, (e) pump, (f) oxygen inlet, (g) water and oxygen outlet. Adapted from [5].

First, the $H_3PMo_{12}O_{40}$ (PMo_{12}) catalyst absorbs light to change the valence state of Mo^{6+} to Mo^{5+} by forming a charge transfer complex with organics as electron and proton donors. This process could be accelerated by photo irradiation and thermal enhancement of sunlight, described in Eq. (1):

$$2Starch - OH + 2[PMo_{12}^{VI}O_{40}]^{3-} \xrightarrow{light\ or\ heat} Starch - O - [HPMo_{11}^{VI}Mo^{V}O_{40}]^{3-} + [HPMo_{11}^{VI}Mo^{V}O_{40}]^{3-} + Oxidized\ \ starch\ \ oligomers \quad (1)$$

Second, the PMo_{12} with Mo^{5+} releases an electron to the anode and an H^+ to the solution, and returns back to its original M^{6+} state. The biomass with long polymeric chains are decomposed and oxidized to small molecular products simultaneously. Finally, electrons reach the cathode and are captured by oxygen to form water with H^+. The overall result is oxidation of organic biomass fuel by oxygen to produce electricity and mediated by photo-catalysis using PMo_{12}, which can be described by following equations:

$$Andode:\quad Starch - O - [HPMo_{11}^{VI}Mo^{V}O_{40}]^{3-} + [HPMo_{11}^{VI}Mo^{V}O_{40}]^{3-} \xrightarrow{anode} 2[PMo_{12}^{VI}O_{40}]^{3-} + Oxidized\ \ starch\ \ oligmers + 2e^- + 2H^+ \quad (2)$$

$$Cathode:\quad 1/2O_2 + 2e^- + 2H^+ \xrightarrow{cathode} H_2O \quad (3)$$

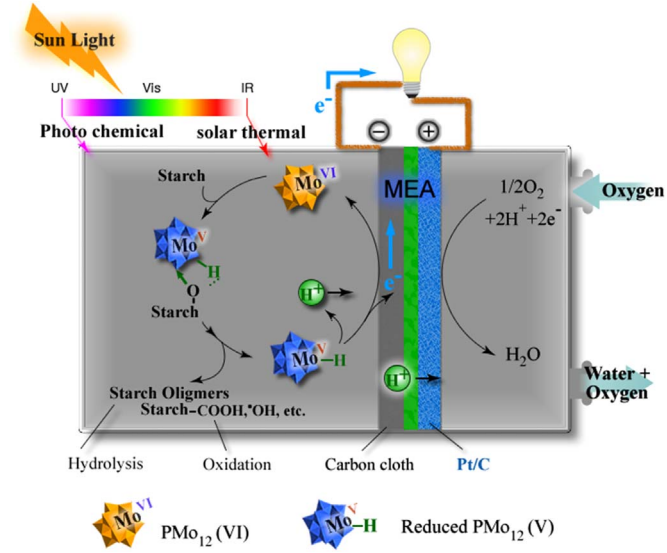

Fig. 7. Voltage and power densities of different biomasses used as the fuels for POM-mediated novel DBFC at 80 °C. Adapted from [6].

Fig. 8. Schematic illustration of the principle of the direct biomass-fueled LCFC with PMo_{12} as the catalyst. Adapted from [5].

4.3.2. Difference from traditional fuel cells

The direct biomass LCFC is a combination of solar cells, fuel cells, and redox flow batteries, but has distinct differences from each.

(1) For a traditional solar cell, light energy is converted to electricity directly via the photovoltaic effect when a semiconductor or dye on the semiconductor is exposed to light [142,143]. However, for the direct biomass-consuming LCFC, short-wave light excites POMs to the excited state and is stored in the form of reduced POMs (i.e., chemical energy) via the photochromic reaction. Moreover, visible and near-infrared light are absorbed by the solution and converted to heat, which can also promote the redox reaction between biomass and POM.

(2) The direct biomass-consuming LCFC also has a similar feature to redox flow batteries [144,145] in that electrolyte solutions with different valence states are used in the electrode cells. But the cathode side is fabricated with a direct oxygen electrode, different from redox flow batteries. Additionally, organic fuel is consumed in LCFC, but organic fuel is not used in a traditional redox flow battery. The overall reaction is the oxidation of organic fuel by oxygen, which does not occur in redox flow batteries.

(3) The cell is different from a traditional PEM fuel cell where catalytic reactions occur on the precious-metal-loaded anode. In direct

biomass-consuming LCFC, the catalytic reactions are mediated by POM solution, but not on the surface of a noble metal electrode. The POM functions as a photo and thermal catalyst and charge carrier takes away electrons from biomass while reducing its own valence state to Mo^{5+} with light irradiation and thermal degradation. The electrons in the POM are then transferred through the external circuit, and the POM reverts to its original Mo^{6+} valence state.

The direct biomass LCFC offers many advantages over conventional fuel cells. This new type of biomass fuel cell uses regenerative POM solutions as catalyst without using a metal-catalyst-based electrode. POM catalysis incorporates the photo-catalysis and thermal degradation of biomass in a single process. Furthermore, POMs are tolerant to most organic and inorganic contaminants because they are robust and self-healing [146]. As a result, the biomass fuels do not require pre-purification treatment, which could substantially reduce fuel cost. In brief, efficient, robust, and economic POM catalyst holds the key to achieving a breakthrough in fuel cell technology.

The biomass-based LCFC is relatively new but shows very promising results. With this groundbreaking technology, raw biomass, such as starch, cellulose, lignin, switchgrass, wood powders, algae, and even city life wastes, can be directly converted to electricity at room temperature [5–8]. High power output has been demonstrated directly using raw biomass without purification or treatment. The catalyst (POM) is extremely stable without contamination. This type of fuel cell is noble-metal-free at the anode. It is expected that biomass-based LCFC can be low cost and suitable for both small power units and large power plants for sustainable energy production from biomass. However, many challenges in both scientific research and commercialization remain.

First, the electrode chemistry needs to be studied to optimize redox reactions on the electrodes. For example, research indicates that the presence of oxygen-containing functional groups on graphite electrodes increases discharging current in a vanadium flow battery [147,148]. However, the electrode chemical modification has not been well investigated in POM discharging fuel cells. In addition, POM acts as both photo-catalyst and charge-carrier in the fuel cell. Transition metal addend POMs are well known to be excited by absorbing light extended to visible wavelength [149,150]. A large number of POMs with different metal components, different structures, or different redox properties can be synthesized and used for degradation of biomass in LCFC. However, most POMs can absorb only low-wavelength light (< 450 nm). To maximally use solar energy to effectively oxidize biomass, POM with strong visible-light absorption should be developed. Moreover, the real chemical reactions between POM and biomass should be fully understood. By understanding the reaction mechanism, high conversion efficiency of biomass to electric power can be achieved.

5. Perspectives

The performance and development stages of biomass-fueled MFC and DBFC are shown in Table 3. MFC show relatively low PD (usually lower than 0.5 mW cm^{-2}), though its operation temperature is low and various biomass-derived substrates can be utilized as fuels. MFC have not been commercialized and face various technical challenges. Lignocellulosic biomass usually needs to be hydrolyzed first to obtain sugar substrates, but the production of lignocellulosic sugar is costly. The production cost of sugar from biomass by enzymatic hydrolysis was estimated at approximately $0.25/kg sugar [151]. However, considering the collection, handling, and transportation of lignocellulosic biomass, the cost may be even higher. As estimated by Rabaey and Verstraete [26], 1 kg of sugar on average contains 4.41 kWh of energy or potentially 13×10^6 coulombs of charge, representing 1.06 kg chemical oxygen demand (COD), which can yield ~1 kWh of useful energy that is worth up to € 0.16 in the European Union. Thus, using lignocellulosic sugars to fuel MFC is not yet economically feasible. A possible solution is to integrate MFC with a biorefinery for integrated ethanol and electricity production—fermentable sugars are used to produce ethanol, while the by-products (such as furfural, phenolic compounds, and fermentative products) are used as fuels for electricity generation. This can enable higher ethanol yields at high biomass loadings in cellulosic ethanol biorefineries, improve water recycling, and provide electricity production up to 25% of total biorefinery power needs [113]. High cost of electrode materials is also a challenge for commercial use of MFC. For air-cathode, a noble metal such as Pt must be used to catalyze the reduction of oxygen. The anodes usually need modifications to increase the biofilm attachment, and cathodes need to

Table 3
Comparison of different lignocellulosic biomass fueled fuel cells operated at low temperatures.

Fuel cell type	Fuels	Operation temperature (°C)	Power density (mW cm^{-2})	Developing stage	Advantage	Technical challenge
MFC[a]	Acetate Sugar Phenolic compounds Biomass hydrolyzate Solid biomass	15–40	0.004–0.2 0.002–0.72 0.0006–0.01 0.01–0.4 0.006–0.05	Laboratory	Mild operation temperature; nearly all biomass components can be used as fuels; possible to direct conversion biomass to electricity	Very low power density; low rate of electricity generation; high internal resistance; high cost of electrode materials
PFC[b]	Soluble biomass, sugar, alcohol	25	0.0001–2	Laboratory	Direct use parts of biomass and wastes	Output of most cell is very low; only can utilize UV light currently
PEMFC[c]	Parts of soluble biomass	25–50	0.004–0.5	Laboratory	Convenient and mild operation	Low power density and efficiency
LCFC[d]	Solid biomass	25–80	0.4–0.7	Laboratory	Direct conversion of solid biomass to electricity without external processing units	Relatively low biomass oxidation efficiency

[a] MFCs have been studied by many groups all over the world for several decades. Well-known groups in MFC study and development include Bruce Logan's group at the Pennsylvania State University; Ioannis Ieropoulos' group at University of the West of England; Derek R. Lovley's group at University of Massachusetts; Jürg Keller's group at University of Queensland; Korneel Rabaey's group at Ghent University; Hanqing Yu's group at University of Science and Technology of China; Xia Huang's group at Tsinghua University; Yujie Feng's group and Aijie Wang's group at Harbin Institute of Technology, etc.

[b] Masao Kaneko's group at Ibaraki University (later institution of the Institute of Biophotochemonics Co. Ltd) in Japan are devoting to developing direct biomass conversion to electricity using photofuel cell technology.

[c] PEMFC are usually fueled by gas fuels such as H_2, or liquid fuels such as methanol. Direct conversion of solid biomass to electricity by conventional PEMFC usually showed very low output power. No well-known group has been found for such research.

[d] Direct conversion of biomass to electricity using liquid catalyst such as polyoxometalates as an electron mediator and PEM as the polymer electrolyte was firstly proposed by Yulin Deng's group at Georgia Institute of Technology.

intensify gas diffusion. The performance of MFC still need improvement. Various issues have been observed even when pure glucose or acetate is used as the substrate. One of the main bottlenecks is the decrease in voltage caused by potential losses, including ohmic loss, activation loss, bacterial metabolic loss, and concentration polarization [152]. Nevertheless, these issues have not been well addressed. Much work is needed to determine the influences of biomass-derived substrates on power output and long-time running performance, cell design, and electrode modification.

DBFC is a promising technology, but it is in early stages at laboratory scale. Direct use of biomass offers a more economic, environmentally friendly, reliable, and sustainable alternative than other utilization pathways, however, it is usually less efficient. The current issues of DBFC mainly include the following: (1) Low power density of less than 1 mW cm^{-2}, far from practical application. (2) Inability to efficiently and completely utilize biomass substrates – The noble metal catalyst used in PEMFC cannot cleave all chemical bonds of biomass substrates. In addition, solid catalysts have low mass diffusion. LCFC seems to solve this problem by using a liquid POM catalyst, but the biomass oxidation efficiency still needs to be improved; (3) Lack of mature technology to cope with the complexity of biomass—Most of the fuel cells are well investigated by fueling with pure chemical fuels, but raw biomass is a highly complex composite containing impurities that can be poisonous to fuel cell catalysts. POM catalysts in LCFC exhibit robust and self-healing property for most inorganic or organic impurities; however, fundamental understanding of the interactions between impurities and POM needs to be developed. For successfully utilizing raw biomass in fuel cells, the catalyst should have the characteristics of (a) oxidizing various organic substrates; (b) efficiently cleaving C-C bonds at low temperatures; (c) efficiently degrading polymers; (d) excellent accessibility to solid biomass fuel; and (e) tolerance to most impurities contained in biomass. Liquid POM catalyst has some advantages for application to DBFC. However, a rational design for power density improvement is necessary in future studies. The structural configuration of the cell has to be well designed to reduce the internal resistance. The kinetics of the electrode reactions has to be investigated in order to maximize power output.

6. Concluding remarks

Lignocellulosic biomass is a promising feedstock for fuel cells because it is renewable, carbon neutral, and sustainable. Biomass can be directly converted to electricity in some recently developed fuel cells; however, it is usually first converted to simple fuels for higher efficiency. MFC and some newly-developed DBFC can be operated at low temperatures. In MFC, biomass is usually first converted to simple carbon sources such as monosaccharides, phenolic compounds, and organic acids, followed by microbial utilization for electricity generation. However, the biomass recalcitrance to sugar release and the inhibitive effects of inhibitors generated during biomass hydrolysis are two major obstacles for the biomass-fueled MFC. The power density of MFC is usually lower than 0.5 mW cm^{-2}, far less than that required for commercial applications. However, they are very well suited for dilute substrate streams such as wastewater. Thus a combination of lignocelluloses biorefinery and waste water treatment using MFC seems to be a promising model for biomass conversion. DBFC refers to technologies that can directly convert polymeric biomass to electricity. This technology shows great promise because biomass can be directly used as a fuel, but it is still in its early stage of development with low efficiency. For improving efficiency of biomass-to-electricity conversion, future research should be focused on biomass processing, electrode development, cell design, parameter optimization, process integration, and an understanding of fundamental process mechanisms.

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