Review on High-Performance Air Cathode Microbial Fuel Cell for Power Generation and COD Reduction

Samuel Reinhard Ignatius Sitorus, Mimi Hani Abu Bakar* & Edy Herianto Majlan
Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

*Corresponding author: mimihani@ukm.edu.my

Received 19 July 2019, Received in revised form 12 November 2019
Accepted 17 January 2020, Available online 30 November 2020

ABSTRACT

The world population is projected to increase by one billion for the next ten years from the year 2016. Unfortunately, global power plants still using non-renewable energy sources. Consumption of fossil fuels harms the environment, while nuclear energy could release a significant amount of radioactive material. Besides the energy issues, the growth in population contributes to the high production of wastewater. Every year, the wastewater treatment industry consumes a high input of energy for treatment purposes. These issues invigorate research interest in microbial fuel cell (MFC) technology that can generate green power electricity while breaking down the organic matter in the wastewater. One of the research advancement in MFC is the air-cathode MFC that is scaled-up friendly due to its simple structure, and ability to utilize the abundance of oxygen in the air as the membrane and scaling up arrangements. Therefore, this review aims to discuss the main positive findings contributing to the recent improvement of air-cathode MFC and the obstacles faced for upscaling.

Keywords: Air-cathode; Microbial Fuel Cell; Power Generation; COD Reduction

INTRODUCTION

In this decade, the consumption of world energy increases each year (Rahimnejad et al. 2011; Rahimnejad et al. 2015). Database from World Bank (2009-2014) showed that world energy produced from fossil energy increased almost 1.5 %/year and projected to increase 2 % for the next five years starting from 2015 (Statistics 2014). This data should be a big concern because fossil energy is non-renewable energy and creates an environmental problem. One of the issues caused by fossil energy is the productions of carbon dioxide (CO₂), which is also the main gas that leads to the greenhouse effect. Data from the National Aeronautics and Space Administration (NASA) showed that global temperature from 2005-2018 increased by 0.8 °C and projected up to 1 °C on 31st December 2020 (Climatic Research Unit 2018).

Furthermore, the growing world population was increasing significantly and projected to increase up to 2.3 billion more people by 2050 or 29 % from an estimated 7.6 billion from 2018 (Population Reference Bureau 2018). The increase in the population directly reflects the increase of global energy consumption and the increase in the production of wastewater. FAO’s AQUASTAT database in 2017, estimated global freshwater withdrawals at 3.928 km³/year (UNITED NATIONS WORLD WATER ASSESSMENT PROGRAMME 2017) estimation up to 44 % (1.716 km³) consumed mainly for agriculture division, while remaining of 56 % (2.212 km³/year) is released into the environment. Thus, replacing fossil energy with a renewable energy source that simultaneously treats the wastewater is essential.

One of the suggested renewable energy systems is the microbial fuel cell (MFC). MFC is a promising technology branched from chemical fuel cells for renewable energy production because it is a direct bio-electrochemical reactor, which realizes the conversion of chemical energy in a microorganism to electricity (Wahab et al. 2018). The microorganisms oxidize the organic substrate to become protons (H⁺) and electrons (e⁻) at the anode side (Logan et al. 2012). The protons released at the anode transferred to the cathode through a membrane, e.g., the Proton exchange membrane (PEM) and cation exchange membrane (CEM), where the combining of these reactions form water (Figure 1) (Kumar et al. 2016). The catalytic microorganisms competent to shuttle the electrons exogenously to the electrode surface or soluble or insoluble electron acceptor without utilizing artificial mediators are referred to as exoelectrogens (Xiao et al. 2014) and are essential for the MFC. MFC offers benefits in terms of energy savings, environmentally friendly, economical, and operational (Li et al. 2014).

At present, there are various MFC systems studied, and each type has a different substrate, method, and configuration. For instance, sediment MFC (SMFC) or benthic MFC (BMFC), has the anode embedded into sediment rich in organic nutrients, while its cathode floating on the ocean surface (Liu et al. 2015). A photo MFC (PMFC) uses microalgae as the inoculum and also gives possible elimination of external air supply when the microalgae placed at the cathode (Wang et al. 2018). There are advanced MFCs such as the Microbial Electrolysis Cell
(MEC), the Microbial Desalination Cell (MDC), and the General Microbial Electrosynthesis Cell (MES). The MEC converts chemical energy stored in organic compounds to hydrogen through biocatalytic oxidation by microorganisms (Hasany et al. 2016; Jafary et al. 2018; Jafary et al. 2017), the MDC is to desalinate saltwater or seawater, and the MES uses the microbe-electrode interaction to steer the microbial metabolism towards increased production of chemicals and fuels (Harnisch et al. 2015).

Consistent improvement is reported from the MFC system to enhance performance efficiency, including the high-cost operating system and low power generation (He et al. 2017). Mostly the researcher uses the conventional dual-chamber MFC as the reactor for the system in MFC (Flimban et al. 2018) (Figure 2). However, dual-chamber MFC configuration has many limitations in research, such as high internal resistance and required large reaction vessels, so it is too tricky to scale up with this configuration (Kakarla et al. 2015; Flimban et al. 2018). Nowadays, researchers show interest in the single-chamber air-cathode MFC system because it is easy to build and easy for scaling up (Tanikkul et al. 2019; Islam et al. 2017) (Figure 2). Besides the simplified structure, a single chamber air-cathode MFC system has a lower system volume and uses abundance oxygen in the air as an electron acceptor to reduce the costs of common catholyte (Bosch-Jimenez et al. 2017). The stacking and submergible air-cathode require the use of air blowers to supplement the oxygen because the prototype is a closed system (Kim et al. 2016).

This review discusses the basic configurations of air-cathode MFC, its progress in gaining high power density and high chemical oxygen demand (COD) removal from wastewater, advancement on both electrodes, membrane, and reactor design until the effort for upscaling from the laboratory setting.

**AIR-CATHODE MICROBIAL FUEL CELL OPTIMIZATION**

**CATHODE AND CATALYST**

Oxygen is a crucial electron acceptor in a single chamber air-cathode MFC system. The reason is that oxygen has a high potential for oxidation reaction resulting in high power generation, in abundance, and low-cost. In air-cathode MFC, the standard material that uses for the cathode mostly carbon-based, such as carbon cloth, J-cloth, carbon rod, carbon felt, and carbon fiber. Carbon material still gives better performance compared to noble metal or metal-based material. Also, carbon material has a high surface area as well as mechanical and electrochemical stability.

Recently, studies in air-cathode MFC using a catalyst in the air-cathode MFC system to increase the reaction rate of oxygen reduction (ORR) and improving power generation performance (Zhao et al. 2017). Platinum (Pt) is a general catalyst that often used with carbon material as an optimal air cathode catalyst for laboratory
MFC (Call et al. 2017). It is well known that Pt-based and its alloys are the best ORR electrocatalyst for now (Pasupuleti et al. 2015). However, the costly Pt-based catalysts limit the application of the air cathode MFC to scale up (Yuan et al. 2015).

The surface-active area of the cathode material is an essential factor in the performance of the ORR catalyst. The more significant surface area of the material, the more activated area sites for the ORR process (Santoro et al. 2017a). It was reported that the specific surface area of the ORR catalyst is related to its catalyst function, which leads to the power generation from the air-cathode MFC system (Zhou et al. 2016). The conventional catalyst applies on the cathode side in the MFC system. The successfulness of these methods in air-cathode MFC system is the activated carbon (AC), and has subsequently attained much attention, as it is cheaper than Pt, has electrocatalytic activity, environmentally friendly, and chemically stable (Zhang et al. 2017). AC material has different physical and chemical characteristics to the other carbon materials, such as carbon black. Generally, the physical characteristics of AC are high surface area, high bulk density, neutral pH, low ash, and low-cost catalyst. However, AC still has some weakness, which is a low electrocatalytic activity (Ahmed et al. 2012). These characteristics perhaps are the critical factors dictating the performance of the air cathode MFC system using AC as a catalyst towards high ORR (Merino-Jimenez et al. 2016; Lv et al. 2019; Zhang et al. 2019).

Irrespective of the AC pore structure, the report has it that the active areas of most catalyst precursors only formed after calcining at moderate temperature, with the active areas located on the inner surfaces of the channel walls. Because of the active areas located in channel walls, the AC degradation caused by peeling, aggregation, and during the operation of the system can be avoided (Li et al. 2014). Several preparation procedures, such as pressing, rolling methods, and spreading methods, were developed to build an air-cathode MFC system. The successfullness of these methods in air-cathode MFC have been reported when paired with AC catalytic layer (CL), gas diffusion layer (GDL) with different structures (Dong et al. 2013; Li et al. 2016; Yang et al. 2015), and electrocatalytic performance of hybrid AC doped with multiple elements (e.g. Copper [Co], Cuprum [Cu], Argentum [Ar]/Silver [Ag], Phosphorus [P], Ferum [Fe]/Iron, Nitrogen [N]) (Liu et al. 2016; Pan et al. 2016; Zhong et al. 2019; Santoro et al. 2019). Other studies have reported that nitrogen and phosphorus-doped carbon materials showed a high ORR activity up to 25 % more than without doped cathode materials (Zhang et al. 2018; Li et al. 2017).

### ANODE

The materials used as anode electrodes must have specific characteristics to improve the interaction performance between microorganism and the anode surface areas (Santoro et al. 2017a). Therefore, an anode material needs to have the following qualities: (1) good electrical conductivity (Rahimnejad et al. 2015), (2) resistance to corrosion (Rahimnejad et al. 2015), (3) high mechanical strength, (4) developed surface area, (5) biocompatibility, (6) environmentally friendly, and (7) low capital cost material (Mustakeem 2015). Common materials possess the above attributes and applied as anodes electrodes for air-cathode MFC system, are the carbon cloth (CC), flexible graphite sheets/plate, graphite felt (GF), graphite rod (GR), graphite granules (GG) and AC (Figure 3) (Merino-Jimenez et al. 2016; Bakar et al. 2016; Tatinaclaux et al. 2018). Recently, many researchers reported on two dimensional (2D) electrode materials such as doping with 2D carbon nanotube (CNT) (Hindatru et al. 2017). However, challenges and problems that arise from a 2D electrode contribute to the low performance of the air-cathode MFC system. The problem that has been studied such as high internal resistance, high ohmic losses, low surface active area and mass transfer over potential which prevent the anode ability to achieve high performance (Sonawane et al. 2017). Despite relatively low-cost materials, stable and showed high conductivity, carbon materials have hydrophobic character, which is unconducive for intense microbial adhesion resulting in poor electron transfer capability and surface fouling by materials from microbial secretion further compounded the problem (Chou et al. 2014). With recent advances in material science and nanotechnology, the three-dimensional (3D) electrode material becomes the attraction in the air-cathode MFC system (Sonawane et al. 2017). 3D electrodes are the electrodes that doped with the 3D structure such as the 3D CNT (Hindatru et al. 2017) or 3D graphene nanosheets (Santoro et al. 2017b) and because of the difference of the structure, the 3D electrode has larger surface area than the 2D electrode. Mostly 3D surface electrode is non-planar electrodes that typically improve the transport of redox species to the electrode surface, increasing current density. Some 3D electrodes are dense, but others are porous or flow-through electrodes whose active surface area is higher than the geometric surface area. 3D surface anodes offer high active areas for efficient colonization of microorganisms and increasing substrate access to the anode respiring microorganism and consequently minimizing mass transfer limitation (Liu et al. 2010). Besides, 3D surface anodes are very critical in adhesion of microorganism communities, high volume to surface ratio, and excellent biocompatibility (Garcia-Gomez et al. 2015).

Recent studies have anode surface-functionalized with nanostructural implements: CNT (Ren et al. 2015; Huang et al. 2015), graphene (GR) (Hou et al. 2014; Najafabadi et al. 2016) and polyaniline/graphene (Huang et al. 2016) and Poly-N-isopropylacrylamide (PNIPAm) (Kumar et al. 2014), to promote the performance of air-cathode MFC system. Diverse nanoengineering methods that are sustainable and environmentally friendly reported assisting in exoelectrogen reaction in the anode side (Rahimnejad et al. 2015). The performance of the air-cathode MFC system could enhance if the composition of the composite anode is good.
The vital purpose of using membrane in air-cathode MFCs is to avoid oxygen in the air to transfer from the cathode chamber to the anode chamber. Previous studies used PEM, Cation Exchange Membrane (CEM) and Polypropylene (PP) felt as a membrane in their single air-cathode MFC system and use ethanolamine as the substrate for the system. They reported that the CEM generated power density, up to 583.7 mW cm$^{-2}$, followed by PEM up to 297 mW cm$^{-2}$, and PP felt up to 268.8 mW cm$^{-2}$ (Song et al. 2015). In other reports, Membrane Electrode Assembly (MEA) prepared through hot pressing catalyst polyacrylonitrile carbon felt (PACF) with pre-treated Nafion 117 (5 cm x 5 cm) and palm oil mill effluent (POME) as the substrate, achieved up to 0.0017 mW cm$^{-3}$ (Islam et al, 2017) while anion exchange membrane (AEM) as the separator with continuous feeding of wastewater generated power density up to 879 mW cm$^{-2}$ (Chen et al, 2018). A study performed on the effect of CEM layers when using wastewater as a substrate in their air-cathode system. They discovered that the system with three membranes achieved more power density than one or two layers of membrane. Three-layer membranes generated maximum power density up to 335 mW cm$^{-2}$, two layers up to 166.23 mW cm$^{-2}$, while one layer up to maximum power of 75.28 mW cm$^{-2}$ (Mohamed et al. 2017). A study done on polyvinyl alcohol (PVA) as the air-cathode MEA and activated sludge as the substrate to remove ethyl acetate (EA), gained maximum power density up to 143 mW cm$^{-2}$ (Liu et al. 2017). From these reported studies, the use of a specific membrane will give different power density results in the system. Mostly the conventional membrane chemical fuel cells are still being used, such as AEM, PEM, and CEM. Nevertheless, there are reports on challenges in applying the ion exchange membrane, i.e., CEM and AEM, including pH splitting, biofouling (Xu et al. 2012; Daud et al. 2018), high oxygen and substrate diffusion. As a result, other low-cost materials that are suitable as membrane: porous cloths, J-cloths, glass fiber, and composite membranes begin to get noticed and investigated as separators in MFC (Yousefi et al. 2016).

Some new materials were reported fit to become the air-cathode membrane and give allowance for the system to scale up. For instance, separator electrode assembly (SEA) developed for the low-cost MFC system in consequence of electrodes evasion contact between the anode and cathode (Zhang et al. 2018). The use of SEA can reduce the internal resistance of the system compared with the Spaced Electrode Assembly (SPA). This suitable strategy could avoid short-circuiting as well as increase the hydrogen transfer between electrodes, which leads to a decrease in coulombic efficiency (Choudhury et al. 2017). A report discussed the SEA membrane placed between the electrodes within 2 cm or less could develop power density output (Cheng et al. 2006). The SEA configuration gained maximum power density up to 280 mW cm$^{-2}$, and SPA configuration gains maximum power density (255 mW cm$^{-2}$).

Recently, many studies have developed many reactor design than using conventional reactor design. Commonly, conventional reactor design of the air-cathode MFC uses cubic shape plexiglass (Wei et al, 2013) or acrylic cube chamber (Tanikkul et al, 2015; Tanikkul et al, 2019), with different volume of the chamber. The effect of the difference reactor design gives different power generation output (Liu et al, 2017) and COD removal. Nowadays, reactor design can be tubular MFC (Estrada-Arriaga et al, 2018) and single chamber rotating air-cathode (Figure 4) (Chen et al, 2018). From Table 1, many studies use conventional design chamber 28 mL plexiglass or acrylic as the reactor for the air-cathode system. A typical design is rectangular, while only a few studies venture on other designs, such as the tubular design and rotating design air-cathode (Chen et al. 2018) (Figure 4). These studies show that the reactor design development of air-cathode MFC still low and still uses a conventional reactor.

The differences in reactor design and size have an impact on power generation and COD reduction. From these studies, the conventional reactor design still gives better performance than the developed design. Due to the low manufacturing cost and simple reactor design, single chamber air-cathode MFC is seemed as suitable for scale-up for practical application (Zhao et al. 2017).

SCALING UP AIR-CATHODE MICROBIAL FUEL CELL

Many efforts on scaling up through air-cathode MFC stacking have been reported (Kuchi et al. 2018). Previous studies constructed a stacked of three tubular air-cathode MFC (t-MFC) vertically using epoxy resin (Liu et al. 2018). The length of the stacking t-MFC is 5 cm, and the diameter is 4 cm, and use PEM as the membrane for the system. They aim to compare the power generation of the air-cathode MFC system when in series and parallel arrangement while using petrochemical wastewater and aromatic hydrocarbon degraders as the substrate. Another study reported a maximum power density obtained when in parallel connection, up to 48.26 mW cm$^{-2}$, compared to 12.7 mW cm$^{-2}$ when in series connection (Liu et al. 2018). The difference in power happened because the parallel connection has more considerable maximum power and lower energy consumption up to 3.8 times than a series connection. However, in COD reduction, the series connection has better performance than a parallel connection.

The series connection also has a higher open-circuit voltage (OCV). Higher the OCV, more pollutants will be removed from the substrate. In another similar study, a reactor was filled with a stack of 40 units air-cathode MFCs within a shared volume of 16 L and assembled with a nonconductive polycarbonate plate. The reactor was divided into four modules of rectangular shape and fed with a mixture of 50 % raw residential wastewater and 50 % anaerobic granular sludge. Their study leads to much higher maximum power density and current density up to...
FIGURE 3. FESEM images of carbon-based material for anode (a) Plain carbon cloth; (b) stainless steel mesh; (c) Plain carbon felt (Merino-Jimenez et al. 2016)

TABLE 1. Advancement Reactor Design For Air-Cathode MFC

<table>
<thead>
<tr>
<th>No</th>
<th>Reactor Design</th>
<th>Power Density</th>
<th>COD (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single Chamber Cubic Shaped (28 mL)</td>
<td>1190 ±10 mW cm²</td>
<td>91±2%</td>
<td>(Wei et al. 2013)</td>
</tr>
<tr>
<td>2</td>
<td>Single Rotating Air-Cathode (150 ml)</td>
<td>879 mW cm²</td>
<td>-</td>
<td>(Chen et al. 2018)</td>
</tr>
<tr>
<td>3</td>
<td>Membrane Free Single Chamber Air-cathode (28 mL)</td>
<td>1895 mW cm²</td>
<td>-</td>
<td>(Wang et al. 2017)</td>
</tr>
<tr>
<td>4</td>
<td>Plexiglass Cylindrical Single Chamber Air-cathode (28 mL)</td>
<td>1911 mW cm²</td>
<td>-</td>
<td>(Liu et al. 2017)</td>
</tr>
<tr>
<td>5</td>
<td>Acrylic Cube Single Chamber Air-Cathode (28 mL)</td>
<td>6.9 mW cm²</td>
<td>62.2%</td>
<td>(Tanikkul et al. 2019)</td>
</tr>
<tr>
<td>6</td>
<td>Tubular Ceramic Air-cathode MFC (16 L)</td>
<td>2500 mW cm²</td>
<td>74%</td>
<td>(Estrada-Arriaga et al. 2018)</td>
</tr>
</tbody>
</table>

2500 mW cm² and 500 mA cm², respectively, in series connection and parallel connection of 5.8 mW cm² and 24 mA cm² (Estrada-Arriaga et al. 2018). While the series connection shows higher output than a parallel connection, there is the issue of voltage reversal when the change from series to parallel connection. The change of the connection made higher parasitic cross current generated in parallel connection. The other studies used tubular ceramic clayware as the membrane and arranged by 3 in one tank reactor with a total volume of 26 L (Figure 5). Every 30 days, each of the anodic chambers of the MFC system changes connection with individual connection, parallel connection, then series connection, and connected with 100 Ω external resistance. The maximum power generation output of each connection gain 2.51 mW cm⁻² for individual connection, 11.46 mW cm⁻³ for parallel connection, and 7.72 mW in series connection (Ghadge et al. 2015).

FUTURE PROSPECTS OF AIR-CATHODE MFC

Air-cathode MFCs have shown interest in bioanode to replace the Pt catalyst. However, recent studies reported on the potential of activated carbon as a substitute for Pt catalyst, though having low conductivity (Ahmed et al. 2012). Nevertheless, the activated carbon has the advantage of having a lower price than Pt, apart from electrocatalytic active, environmentally friendly, and chemically stable (Zhang et al. 2017).

The application of the conventional membrane (PEM, CEM, and AEM) also exhibited weakness during durability study. Apart from its high price and overrated application in MFC, these conventional membranes succumb to biofouling. However, studies find that the biofouling issue can be dealt with through in-situ cleaning or only using non-conventional material as membranes. Unfortunately, reports are showing no apparent improvement in power performance of air-cathode after the in-situ cleaning done to the conventional membrane, (Rossi et al. 2018; Vogl et al. 2016)

Another way to increase the power performance of the air-cathode MFCs would be through the system design. Stacking the air-cathode single cells either in the series or parallel arrangements, would be essential to significantly increase the power generation and also increase the COD removal of the air-cathode MFC reactor. Furthermore, attention should focus on the voltage reversal that occurs during the stacking system arrangement on the air-cathode MFC system.
There are broad real-world application potential waiting for air-cathode MFC if the cost and the low power generation issues could be solved, especially in harvesting renewable energy from wastewater, waste biomass, and other organic waste matter.

CONCLUSION

Researchers are trying to find the best suitable renewable energy to overcome the world energy crisis. Renewable energy as the MFC system is a new promising energy source that deems suitable to replace the traditional fossil energy. The air-cathode MFC, a subset of MFC, has a simple design that makes it easy for scaling up to suit its application. Air-cathode MFC also has many advantages: the most feasible, practical, and cost-effective configuration for power generation and wastewater treatment. Many studies on invention and advancement did improve air-cathode MFC such as electrode and membranes from extensive materials, modification of anode, design reactor development from lab scale to application and stacking arrangements. These advancements are to boost up the performance of air-cathode MFC as one feasible alternative energy that can be scaled up from lab scale to application.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support given for this work by GUP-2018-012 from Universiti Kebangsaan Malaysia.

DECLARATION OF COMPETING INTEREST

None.

REFERENCES


FIGURE 5. Schematic Stacking air-cathode MFC; (a) Individual Connection; (b) Series Connection; (c) Parallel Conexction (Ghadge et al, 2015)


