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"Gheorghe Asachi" Technical University of Iasi, Romania



A BRIEF REVIEW ON RECENT ADVANCES IN AIR-CATHODE MICROBIAL FUEL CELLS

Pritha Chatterjee¹, Makarand Madhao Ghangrekar^{1*}, Donal Leech²

¹Department of Civil Engineering, Indian Institute of Technology, Kharagpur – 721302. India ²School of Chemistry, National University of Ireland Galway, University Road, Galway, Ireland

Abstract

The performance of cathode affects the overall performance of a microbial fuel cell (MFC), and cathode configuration affects the fabrication cost of this bioelectrochemical system in a large way. Various modifications in cathode structures have been observed in MFCs. Among them air-cathode MFCs are considered to be the most efficient and sustainable option due to elimination of aeration, as required in aqueous cathodes which consumes energy and increases operating cost of MFCs. An air cathode usually consists of (a) a conductive base material, (b) current collectors, (c) catalyst layer, (d) binder layer, and (e) diffusion layer. In this article the recent advances made in fabrication of air-cathode MFC are reviewed. The advantages and disadvantages of different materials used for preparation of an air-cathode are analyzed. On-field application of MFC is limited even after a decade of extensive research. This article also presents the challenges incurred in scaling-up of an MFC for real field application. In addition, this review will assist to realize the advantages and disadvantages of different materials used in construction of air-cathodes. This knowledge will help in intelligent selection of materials for fabrication of air-cathode MFC in future and will further aid to achieve a competitive technology for electricity harvesting while treating wastewater.

Key words: air-cathode, binder, catalyst, current collector, microbial fuel cell

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1. Introduction

A microbial fuel cell (MFC) represents a technology that has the potential to address the problems of energy crisis and environmental pollution at the same time, as energy is recovered in the form of direct electricity for onsite use during treatment of wastewaters (Angenent et al., 2004; Pant et al., 2016). Habermann and Pommer (1991) did a pioneering work in using MFC as a wastewater treatment system. A MFC is a bioreactor incorporated with electrochemical system that converts chemical energy into electrical energy (Du et al., 2007). The organic matter from the wastewater is converted to carbon dioxide in the anodic chamber under anaerobic conditions. Pant et al., (2010a) reviewed the different types of substrates that can be used in MFCs and concluded that MFCs are capable of treating many complex wastes like pharmaceutical waste, biorefinery waste etc. During this oxidation of organic matter, the electrons released reduce the anode, and migrate through the external circuit towards the cathode. The device intended to be powered is attached to this external circuit. Protons move from anodic chamber to cathodic chamber through a proton exchange membrane. On the cathode the oxidant, generally oxygen is reduced to form water. Thus, carbon neutral energy liberation in the form of direct electricity is possible using wastewater as a fuel in MFC.

Although there has been marked improvement in the performance of MFC through research, large scale practical applications of MFCs are yet to be achieved. The main constraints for practical

^{*} Author to whom all correspondence should be addressed: e-mail: E-mail: ghangrekar@civil.iitkgp.ac.in; Phone: +91-3222-283440; Fax: +91-3222-282254

application of MFCs are high fabrication cost and low energy conversion efficiency (Li et al., 2010; Oliveira et al., 2016; Zhang et al., 2010b). Rozendal et al., (2008) estimated capital costs for fabrication of MFCs, based on materials currently being used in the laboratory. They showed that the price of electrode materials and separator can account for the 57% of total capital cost. Hence to reduce the capital cost, it is necessary to design efficient electrodes and search/synthesize cheaper electrode and separator materials. The material selected for separator should be effective in proton transfer, should minimize substrate diffusion from anode to cathode and also oxygen diffusion from cathode to anode (Alvarez-Gallego et al., 2012). The material selected for electrode should offer higher specific surface area, and cathode material should have lower oxygen reduction overpotential (Sevda et al., 2013).

There are a number of review articles describing various aspects of MFC. However, most of them are based on particular topics like non-platinum based catalyst (Ben Liew et al., 2014), nano-carbon as electrode material (Ghasemi et al., 2013a), graphene based electrodes (Wang et al., 2013), anode architecture (Kumar et al., 2013), and overall development of MFC (Bullen et al., 2006; Du et al., 2007: Logan et al., 2006a: Oliveira et al., 2013a: Rabaey and Verstraete, 2005). Power output of a MFC can be increased by improving performance of the cathode (Liu and Logan, 2004). Researchers have thus focused on the performance of cathode as the most challenging aspect of MFC design (Zhang et al., 2011b). A MFC configuration consisting of an anode and a cathode chamber separated by a proton exchange membrane (PEM) is difficult to implement on a large scale (Kim et al., 2009). Therefore, researchers are focusing on simpler reactor design to overcome this problem. For example, single chamber air cathode MFCs have been studied, where the cathode does not require placement in water (Ahmed et al., 2012; Cheng et al., 2006; Duteanu et al., 2010; Feng et al., 2011; Kim et al., 2009; Liu and Logan, 2004; Logan et al., 2006b). Elmekawy et al., (2013) reviewed the different challenges and potential opportunities of microfluidic microbial fuel cells and mentioned that these micro-sized MFCs offered lower internal resistance. In this article, the recent advances in air cathode MFCs are explored. To overcome the difficulties in scaling up of MFCs, the challenges that need to be addressed for practical implementation are also discussed.

2. Single chamber MFC: Advantages and disadvantages

In an attempt to minimize the operating cost of MFCs air breathing single chambered MFCs were developed by researchers. The major reaction that takes place at the cathode is reduction of oxygen. The solubility of oxygen (mole fraction basis) in water is only $4.6*10^{-6}$ at 25 °C, while that in air it is 0.21 (Logan, 2008; Wei et al., 2011). Because of this,

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oxygen reduction reaction at aqueous cathode is restricted due to limited availability of oxygen. The single-chambered air cathode offers several advantages over two-chambered systems such as: (a) the catholyte does not need to be aerated, oxygen in the air can directly react at the electrode, (b) recycling or chemical regeneration of the catholyte is not required, (c) higher volumetric power density is easily achievable due to smaller cell volume (Liu and Logan, 2004), and (d) the overall volume and footprint of the MFCs will be less in air cathode configuration due to elimination of a cathodic chamber.

In spite of these advantages offered by aircathode MFCs, there are certain disadvantages related mostly to the materials used in construction. The major disadvantages associated with air-cathode MFCs are (a) fouling of the cathode surface exposed to air, (b) diffusion of oxygen into anodic chamber, (c) electrolyte loss due to evaporation (Wei et al., 2011), (d) necessity of a catalyst on cathode for enhancing oxygen reduction reaction (Freguia et al., 2007), and (e) requirement of a binder. This review attempts to elaborate the advantages and disadvantages of different materials used in construction of aircathodes. This knowledge will help in intelligent use of materials for making different components of air cathode MFC in future.

3. Components of air cathode

The separator has anolyte on one side and it is exposed to air on the other side. An air cathode usually consists of (a) a conductive base material, (b) current collector, (c) catalyst layer, (d) binder layer, and (e) diffusion layer (Wei et al., 2011).

3.1. Conductive base materials

The base material for the electrode provides a conductive path to the external circuit. To function as a good electrode, a material should have the following properties namely (a) good conductivity, (b) high chemical stability, (c) high mechanical strength, and (d) low cost (Sharma et al.). Carbon in paper or cloth form is the most widely used material in air cathodes (Ahmed et al., 2012; Cheng et al., 2006; Martin et al., 2011; Shi et al., 2012; Sun et al., 2009; Zhang et al., 2009b). Although carbon is not very conductive, its stability and lack of reactivity makes it a suitable electrode material. However, carbon cloth is expensive (Zhang et al., 2010a) and longtime stability of carbon paper is doubtful due to the brittleness of the material.

Electrodes made of metals and alloys such as stainless steel (SS) can also be used. For example, Zhang et al. (2011b) constructed a cathode by impregnating carbon powder around a stainless steel mesh and obtained a power density of 1616 mW/m^2 . Simple or modified carbon powders are also being increasingly used as electrode materials (Duteanu et al., 2010). Zhuang et al., (2010) applied a nickel (Ni) based paint and manganese dioxide (MnO₂) catalyst to

carbon cloth and obtained a volumetric power density of 11 W/m³. This carbon cloth served as both a membrane and the base material for the cathode. It showed a high proton diffusion rate, reduced the internal resistance and gave higher power output. Sun et al., (2009) obtained a power density of 878 mW/m³ using a platinum catalyst on carbon paper as cathode. Martin et al., (2011) used a platinum (Pt) catalyst on carbon paper cathode and obtained a power density of 90 W/m³.

This suggests, in spite of same cathodic material used, the power output obtained is different due to several reasons like differences in the MFC configuration, catalyst loading, anolyte composition, mode of operation, temperature, pH etc. Performance of some air cathode MFCs using different materials for cathodes are listed in Table 1 through Table 4. An air cathode MFC (Fig. 1) is prepared by impregnating the conductive electrode material, with or without catalyst, to enhance oxygen reduction reaction on the exposed surface of membrane separator, provided with an appropriate current collector.

3.2. Current collectors

Although carbon based electrodes are extensively used in MFCs, these materials have very low electrical conductivity. This can contribute to increased ohmic losses in larger anodic volume (Zhang et al., 2010b). Rozendal et al., (2008) reported that the electrical resistance of graphite is 1375 $\mu\Omega$ cm, while that of the metal titanium is 42 $\mu\Omega$ cm. Inclusion of a metal current collector on the cathode surface can ensure proper distribution of current and also reduces the ohmic losses (Zhang et al., 2010b). Zhang et al., (2011b) used commercially available stainless steel (SS) mesh with varying characteristics as current collectors and found that MFC performance varies as a function of the current collector. The performance of MFCs using different current collectors is compared in Table 1. For example, Zuo et al. (2008) pressed a SS mesh against the cathode and the internal resistance decreased from 47 Ω (without current collector) to 29 Ω .



Fig. 1. Schematic representation of an air-cathode MFC

Fable 1. Performance comp	parison of	f MFCs using	different c	current colle	ectors
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Cathode	Anode	Membrane	Current collector	Binder	Diffusion layer	Catalyst	Max. power density	Prepared by
Carbon powder	Graphite fiber brush	Not mentioned	SS mesh	Not mentioned	2 layers of PDMS	Pt	$\frac{1616\pm25}{mW/m^2}$	Zhang et al., (2011b)
Activated carbon powder	Graphite fiber brush	Not mentioned	Ni mesh	PTFE	1 layer of PTFE	Pt/Pd	1415 mW/m ²	Zhang et al., (2009b)
Graphite	Graphite	Nafian	SS mesh	Nafian	Not	C-TMDD	$\begin{array}{c} 574\pm51\\ mW/m^2 \end{array}$	Zuo et al.,
paint on AEM	fiber brush	Nation	No collector	Nation	mentioned	COIMPP	$\begin{array}{c} 449 \pm 35 \\ mW/m^2 \end{array}$	(2008)

The maximum power produced increased by 28% compared to the same system without the mesh. Other metals like titanium (Duteanu et al., 2010) and nickel (Zhang et al., 2009b) have also been used. Air cathode MFCs employing more uniformly spread current collector like a sock net give more consistent and dependable results for future use, and it is reported to produce power density of 3.2 times higher than the MFC having similar configuration but provided with SS wire as current collector (Chatterjee and Ghangrekar, 2014).

3.3. Catalyst

Use of an air cathode eliminates the problem of low aqueous solubility of oxygen, by direct diffusion of oxygen to the cathode. The oxygen reduction reaction (ORR) however has a high overpotential for reduction to water (Freguia et al., 2007). To overcome this problem catalysts are often used on cathode surface. Use of catalyst on the cathode helps in: (a) increasing the affinity of the cathode to oxygen, and (b) decreasing the activation energy of ORR (Duteanu et al., 2010). A catalyst layer is applied on the surface of cathodes by spray paint gun or brush. The catalysts generally used in air cathode MFC can be grouped into three types: noble metal catalyst, non-noble metal catalyst and activated carbon powder.

3.3.1. Noble and non-noble metal catalysts

Platinum (Pt) is the most widely used cathode catalyst; however, it is very costly and moreover it has poor ORR kinetics in neutral pH and at lower temperature (Duteanu et al., 2010). Some other catalysts like Co-tetra-methyl cheaper phenylporphyrin (CoTMPP) (Zuo et al., 2008), iron phthalocyanine (FePc) (Cheng et al., 2006; Sun et al., 2009) and manganese dioxide (Zhang et al., 2009b; Zhuang et al., 2010a) are also used. Zuo et al., (2007) showed that a tube cathode MFC with two CoTMPP coated tubes produced slightly less power (8.8 W/m³) than that obtained with a carbon paper cathode with Pt catalyst (9.9 W/m³) (Table 2). Zuo et al., (2008) measured the performance of CoTMPP as catalyst and found that both power and Coulombic efficiency (CE) of MFC increased proportionately with the catalyst loading. Longer operation times were needed as the catalyst loading was decreased, allowing more oxygen to diffuse through the cathode into the electrolyte. This oxygen was used by bacteria for aerobic degradation of the acetate substrate, lowering the electron recovery and therefore decreasing the CE (Zuo et al., 2008).

Ghasemi et al., (2013b) used copper pthalocyanin (CuPc) and Ni nanoparticles and observed CuPc to be performing almost similar to Pt catalyst followed by Ni nanoparticles. Use of nanoparticles in cathode as catalyst increases the effective surface area for ORR, thus improving its performance. However, use of such metals like copper or nickel needs further investigation for long-term stability to operate MFCs for a long time. There is a possibility of leaching of these metals into the catholyte and thus creating toxicity for the microbial population hence reducing the opportunity and advantage of biocathode formation in the MFC. A new type of binder-free gas diffusion electrode made of cobalt oxide (Co₃O₄) micro-particles directly grown on stainless steel mesh (SSM), by using an ammonia-evaporation-induced method, demonstrated improved performance in terms of electrocatalytic activity, selectivity, durability and economics toward ORR in pH-neutral solution, in comparison with conventional carbon supported platinum catalyst (Gong et al., 2014).

3.3.2. Activated carbon powder

Carbon is generally considered an inert material; however, it has some superficial activity due to the presence of heteroatoms such as oxygen, hydrogen, sulphur, nitrogen, etc. The activity of carbon can be increased by optimizing the proportion of these atoms on the carbon surface. Activated carbon powder thus produced can be used in place of other ORR catalysts (Duteanu et al., 2010; Harnisch et al., 2009; Pant et al., 2013; Pant et al., 2010b; Zhang et al., 2009a; Zhang et al., 2011a). These non-metal catalysts are more stable than the commonly used platinum (Shi et al., 2012). An air cathode MFC using N-doped carbon powder prepared by nitric acid (HNO₃) refluxing after heat treatment and acid treatment was prepared by Shi et al. (2012) and their performance was compared to a MFC using Pt catalyst on cathode. Threefold increase in power, comparable with platinum catalyzed cathode, is reported using treated carbon as compared to the untreated carbon. Besides nitric acid refluxing, N-doped carbon powder can also be synthesized by chemical vapor deposition (Feng et al., 2011) and sol-gel polymerization (Jin et al., 2011). Dong et al., (2012) prepared an air cathode by rolling activated carbon (AC) and polytetreafluoroethylene (PTFE), combined in different ratios. Maximum power density was obtained for AC to PTFE ratio of 6 (802 mW/m²) and lowest power density was obtained for a ratio of 11 (584 mW/m²). Duteanu et al., (2010) prepared an air cathode by coating a polymer electrolyte membrane with acid treated carbon powder and compared its performance in MFCs using cathodes prepared by coating the same membrane with untreated carbon with and without Pt catalyst; and comparable performance in the MFC using acid treated carbon powder to the Pt/C cathode was reported. At lower current densities the Pt/C cathode performed better, while the acid treated carbon powder cathode had a comparable performance with Pt/C electrode at higher current densities.

Recently, a porous nitrogen-doped carbon nanosheet was used as an alternative to Pt catalyst in a MFC (Wen et al., 2014), which gave a higher power density than a Pt catalyst. A higher volumetric power obtained with polypyrrole (PPy) compared with conventionally used Vulcan XC exhibits that PPy is a better conductive support to ORR (Khilari et al., 2014). Cost effective manganese dioxide nanotube/graphene composites are reported to demonstrate high ORR activity and high power generation ability, hence making it a potential cathode

material for the replacement of expensive Pt in constructing large-scale MFC for wastewater treatment and bioelectricity production (Khilari et al., 2013a) (Table 2).

Table 2. Performance of MFCs	using different	cathode catalyst
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Cathode	Anode	Membrane	Current collector	Binder	Diffusion layer	Catalyst	Max. power density	Prepared by	
Carbon			conceior		luyer	No catalyst	102 mW/m^3	Uy	
cloth coated	Graphite	CEM	Not	PVDF	Not	MnO ₂	$\begin{array}{c} 466 \pm 25 \\ mW/m^3 \end{array}$	Zhang et al.,	
with graphite paint	granules		mentioned	inclutioned		Pt	$\begin{array}{c} 726\pm25\\ mW/m^3 \end{array}$	(2009b)	
Ni based paint	Graphite granules	Carbon cloth	Not mentioned	PTFE	Not mentioned	MnO ₂	11 W/m ³	Zhuang et al., (2010)	
Carbon paper	Carbon paper	Microfiltration membrane	Not mentioned	Not mentioned	PTFE	Pt	878 mW/m ³	Sun et al., (2009)	
Graphite paint	Graphite fiber brush	CEM	Not mentioned		Not mentioned	CoTMPP	449 mW/m ³	Zuo et al., (2008)	
Graphite	Carbon	Ultrafiltration	Not		Not	CoTMPP	8.8 mW/m ³	Zuo et	
paint	paper	membrane	mentioned	Nafion	mentioned	Pt	9.9 mW/m ³	al., (2007)	
Carbon cloth						Pt	480 mW/m ²	Chang at	
Carbon cloth	Carbon cloth	Not mentioned	Not mentioned	Nafion	Not mentioned	CoTMPP	369 mW/m ²	al.,	
Carbon cloth						No catalyst	93 mW/m ²	(2000)	
						C-CoOx	$\begin{array}{c} 554\pm27\\ mW/m^2 \end{array}$		
Carbon	Carbon		Not	Not	Not	C-FePc	$\begin{array}{c} 412\pm20\\ mW/m^2 \end{array}$	Ahmed et	
cloth	cloth	Not mentioned	mentioned	mentioned	mentioned	C-CoOx-FePc	$\begin{array}{c} 654\pm32\\ mW/m^2 \end{array}$	(2012)	
						Carbon powder	$\begin{array}{c} 271 \pm 13 \\ mW/m^2 \end{array}$		
						Untreated	310.8 + 15		
						carbon powder	mW/m ²		
Carbon	Carbon	Not mentioned	Not	Nation	4 PTFE	Treated	9347+5	Shi et al.,	
cloth	brush	Not mentioned	mentioned	Ivalion	layers	carbon	mW/m^2	(2012)	
						Pt/C	980.5 ± 7		
						Pt	90 W/m^3		
Carbon	Carbon	Leloth	Not	Nation	PTFF	Mn ₂ O ₃	32 W/m ³	Martin et	
paper	felt	J-CIOUI	mentioned	Ination	TIFE	Fe ₂ O ₃	15 W/m^3	(2011)	
-					DTEE	С	8 W/m ³	Dong at	
SS mesh	Carbon mesh	Not mentioned	Not mentioned	Not mentioned	PTFE+ Carbon powder	AC + PTFE	802 mW/m ²	al., (2012)	
Ch	Cert	Poly-				HNO ₃ treated carbon	170 mW/m^2	Duteanu	
powder	felt	felt dectrolyte membrane	Ti mesh	Nafion	PTFE	Untreated carbon	51 mW/m ²	et al., (2010)	
						Pt	217 mW/m ²		
Carbon	Carbon		Not	Not	Not	Carbon black	37.9 mW/m ²	Ghasemi	
powder	Paper	Nafion 117	mentioned	mentioned	mentioned	Ni/C	94.4 mW/m ²	et al., (2013b)	
							Pc/C	56 mW/m ²	< /

						CuPc/C	118.2 mW/m ²	
						Pt	120.8 mW/m ²	
Carbon	Carbon	Not montioned	SS not	Not	DTEE	PNCN	1159.34 mW/m ²	Wen et al. (2014)
powder	brush	Not mentioned	55 liet	mentioned	FIFE	Pt	858.49 mW/m ²	
SS mash	Carbon	Not montioned	SS not	Nation	4 layer	Pt	21.2 mW/m ³	Gong et
55 mesn	cloth	Not mentioned	55 liet	Nation	Teflon	Co ₃ O ₄	17.8 mW/m ³	al. (2014)
						MnCo ₂ O ₄ /PPy	6.11 mW/m ³	
Carbon cloth	Carbon cloth	Nafion	Not mentioned	Not mentioned	Not mentioned	MnCo ₂ O ₄ /C	4.22 mW/m ³	Khilari et al. (2014)
ciotii						С	1.77 mW/m ³	

3.4. Binder

To apply the catalyst layer properly to an electrode surface or to apply carbon powder on the separator surface, with or without catalyst, a binder is required. Polymer such as Nafion (Cheng et al., 2006; Duteanu et al., 2010; Martin et al., 2011; Shi et al., 2012; Zhang et al., 2009b; Zhuang et al., 2010; Zuo et al., 2007) is the most commonly used binder. Nafion is most suitable for use as a binder due to its high proton conductivity (Zhang et al., 2012). The high cost of Nafion (\$ 667/m²) has resulted in research to find cheaper alternatives to it (Zhang et al., 2012), such as polytetrafluoroethylene (PTFE) (Cheng et al., 2006; Zuo et al., 2008), polyvinylidene fluoride (PVDF) (Zhang et al., 2009b), polydimethyl siloxane (PDMS) (Zhang et al., 2012; Zhang et al., 2010a), etc. Cheng et al., (2006) found that power density in MFCs decreases with use of PTFE in place of Nafion, but observed a more stable performance in the MFC using the PTFE binder. Wang et al., (2010) mixed PTFE and Nafion in different ratios and used them as binders; and observed increased power density with an increase in percentage of Nafion in the mixture. Nafion is a polymer, which is conductive to protons having both hydrophilic and hydrophobic domains along with a transition zone. On the other hand, PTFE is a highly hydrophobic material that can reduce electrolyte loss from the anode chamber and have good resistance to oxygen transfer across the material. It is however not an electrolyte. As PTFE is highly hydrophobic it also causes the cathode catalyst to become too dry, thus limiting effective proton transfer (Cheng et al., 2006).

Zhang et al., (2009b) used a polyvinylidene fluoride (PVDF) binder and obtained a maximum power density of 726 mW/m³ using Pt catalyst (Table 2). Saito et al., (2010) explored the possibility of using non-ionic hydrophobic polyphenylsulphone (PPS) as binder of cathode catalyst. The PPS material was sulphonated to different degrees and best performance was reported in the MFC with the non-ionic nonsulphonated binder. It was inferred that the presence of sulphonate groups in the binder reduced the oxygen reduction capacity of the cathodes by adsorption of the sulphonate groups to the active sites on the catalyst and also by hampering proton diffusion. Zhang et al., (2012) examined hydrophobic polydimethylsiloxane (PDMS) as an anti-flooding catalyst binder in MFC cathodes.

Although all these binders used as alternatives to Nafion initially had a lower performance, they had almost equivalent performance after long-term use (Cheng et al., 2006; Saito et al., 2010; Wang et al., 2010; Zhang et al., 2012). Moreover, as Nafion is an expensive material it may bring economic limitation in full-scale application of MFC systems. Although the cheaper binders, such as PDMS, produce about 23% less power compared to Nafion, their use will reduce the production cost of MFC, for example PDMS costs around only 0.23% of that of Nafion (Zhang et al., 2012).

3.5. Diffusion layer

A hydrophobic layer is usually applied to the air breathing side of the cathode to reduce diffusion of oxygen into the anode chamber and also to reduce electrolyte loss from the anode chamber due to evaporation (Wei et al., 2011). Cheng et al., (2006) obtained higher CE and power densities after applying successive layers of PTFE as a diffusion layer. This reduced electrolyte loss from the anode chamber. Whilst successive addition of diffusion layers increased the CE, the power density diminished after a certain number of layers due to lower availability of oxygen at the cathode. Power density was reported to be increased by 42% and CE by 200% compared to that for commercially available cathodes.

Zhang et al. (2010a) used PDMS as a diffusion layer. It is stable, hydrophobic and less expensive than PTFE. Maximum power density of 1635 mW/m² was reported with three layers of PDMS and a carbon cloth cathode. Generic plastic wrap was also used as diffusion layer by Hays et al., (2011) to obtain a power density of 150 mW/m². They found a problem that a liquid layer was formed between the cathode and the diffusion layer. This liquid layer reduced oxygen mass transfer from gaseous phase to liquid phase, thereby giving a lower performance of the MFCs. Performances of MFCs using different binders are summarized in Table 3. Best performance (766 mW/m^2) was observed using four diffusion layers on the cathode surface (Table 4). Zhang et al. (2011b) compared the long-term performance and stability of MFCs having cathodes with diffusion layers of varying porosity. They observed that although initially the power production was greater in the MFC with higher porosity of diffusion layer, after one year its performance decreased by 40%, unlike MFCs with lower diffusion layer porosity whose performance decreased by only 20%. Liu et al., (2011) prepared a novel air cathode MFC using a hydrophobic doublesided cloth as the base material for cathodes without any diffusion layer. This decreased the cost and simplified the manufacturing of cathodes. However, long-term stability of this configuration needs to be evaluated.

Table 3. Performance of MFCs under different binders

Cathode	Anode	Separator	Binder	Diffusion layer	Catalyst	Max. power density	Prepared by
Carbon	Graphite		Nafion	4 PTFF		1790 mW/m ²	Saito et al
powder on carbon cloth	fiber brush	Carbon cloth	PPS	layers	Pt	1660 mW/m ²	(2010)
Carbon	Carbon	Carbon aloth	Nafion	Not	D+	480 mW/m^2	Cheng et
powder	cloth	Carbon cioui	PTFE	mentioned	Γι	360 mW/m ²	al., (2006)
Cu mash			Nafion			2220 mW/m ²	
Cumesn	Graphite		PDMS		D+	1710 mW/m ²	Zhang et
SS mash	fiber brush		Nafion		Γι	1840 mW/m ²	al., (2012)
55 mesn			PDMS			1680 mW/m ²	
			PDMS			1060 mW/m ²	
			PTFE			549 mW/m ²	
Carbon cloth	Carbon cloth	Not mentioned	Nafion + PTFE (3:2)	4 PTFE layers	Pt/C	685 mW/m ²	Wang et al., (2010)
			Nafion + PTFE (2:1)			844 mW/m ²	

Fable 4.	. Performance	e of MFCs	under	different	diffusion	layers
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Cathode	Anode	Membrane	Binder	Diffusion layer	Catalyst	Max. power density	Prepared by
				2 layers of plastic wrap		$\frac{150 \pm 22}{mW/m^2}$	
Activated carbon	Carbon mesh	Pulp laminated	Not mentioned	1 layer of	Not mentioned	110 ± 14 mW/m ²	Hays et al., (2011)
Curbon	mesn	glubb Hoer	mentioned	PDMS	mentioned	140 ± 6.4 mW/m ²	(2011)
				1 PDMS layer		1592 ± 19 mW/m ²	
SS mesh				2 PDMS layer		$1610 \pm 56 \text{mW/m}^2$	
	Graphite fiber brush	Not mentioned	Not mentioned	3 PDMS layer	Pt	1010 mW/m ²	Zhang et al., (2010b)
Carbon				1 PDMS layer		1553 ± 19 mW/m ²	
cloth				3 PDMS layer		1635 ± 62 mW/m ²	
				4 PTFE layer		766 mW/m ²	
Carbon	Carbon	Carbon cloth	Nafion	8 PTFE layer	Pt	$\begin{array}{c} 633 \pm 7 \\ mW/m^2 \end{array}$	Cheng et al.,
powder	ciotii			No layer		$\begin{array}{c} 538\pm 6\\ mW/m^2 \end{array}$	(2000)
Activated	Graphite	Not montioned	Not	70 % porous layer of PTFE	Not	$\begin{array}{c} 734 \pm 18 \\ mW/m^2 \end{array}$	Zhang et al.,
carbon	fiber brush	not mentioned	mentioned	30 % porous layer of PTFE	mentioned	$\begin{array}{c} 789\pm68\\ mW/m^2 \end{array}$	(2011b)
Double sided cloth	Carbon	N-4 montioned	Not	No layer	Pt-C	$\begin{array}{c} 0.7\pm0.02\\ mW/m^2 \end{array}$	Liu et al.,
Carbon cloth	cloth	inot mentioned	mentioned	4 PTFE layers	Pt-C	$\begin{array}{c} 0.66 \pm 0.01 \\ mW/m^2 \end{array}$	(2011)
Carbon cloth	Carbon cloth	Micro-fiber cleaning cloth	Not mentioned	Polyolefine membrane	Pt	750 mW/m^2	Tugtas et al., (2011)

Tugtas et al., (2011) used cheaper spunbonded polyolefin sheet as a diffusion layer in place of PTFE and obtained a power density of 750 mW/m² using a carbon cloth cathode. Successful application of such cheaper material will contribute in bringing down the production cost of MFC and enhancing its economic viability for full-scale application.

4. Membrane Electrode Assembly (MEA)

In a conventional MFC the anodic and cathodic compartments are separated by a membrane and placed in respective electrodes are these compartments. This increases the distance between cathode and anode and simultaneously increases the length of the path required to be traversed by a proton thus increasing the internal resistance of the system (Wei et al., 2011). Construction of MFCs where this distance can be minimized may therefore provide for devices with higher performance. Reactor designs with electrodes placed on either side of the membrane are known as membrane electrode assembly (MEA) MFCs (Hays et al., 2011; Zhang et al., 2011b). Implementation of MEA-MFCs have improved the overall reactor performance and reduced the capital cost considerably (Kim et al., 2009; Liu and Logan, 2004; Zhuang et al., 2010).

MEAs are generally constructed by the following two steps: (a) hot pressing the membrane with the elctrodes to obtain close contact between the membrane and the electrodes (Prakash et al., 2010; Zhuang et al., 2010), and (b) applying a conductive layer, with or without catalyst, to the surface of the separator by a spray paint gun (Zhuang et al., 2010). Catalysts are usually applied on that side of the cathode which is facing the membrane (Prakash et al., 2010). Complete contact between the electrodes and the membrane is a strict requirement for MEA constructed by this method, which makes it difficult for implementation of larger volume MFCs in field due to limitations of substrate diffusion (Zhuang et al., 2010). Moreover, this method is only suitable for Nafion-electrode assemblies or materials that can withstand high temperature and not for other cheaper alternatives where thermal degeneration might occur (Kim et al., 2009). This increases the cost of the entire setup as we try to scale up the MFCs. To avoid this problem Zuo et al., (2007) constructed a new type of membrane electrode assembly by coating a membrane with graphite paint and furthur coating it with a catalyst. Duteanu et al., (2010) also used the same procedure to prepare a membrane electrode assembly. Kim et al., (2009) applied a layer of hydrophilic hydrogel between the membrane and the cathode which improved the performance by increasing hydration and maintaining proper contact between the membrane and electrode.

Zhuang et al., (2010) compared the performance of different membrane-cathode assemblies (MCA) and cloth-cathode assemblies (CCA) in MFCs, to find an optimum cathode configuration for scaling up of MFC. Carbon cloth containing catalyst was hot pressed to an ion exchange membrane to prepare the MCAs. To prepare the CCA a nickel based conductive paint and a catalyst was sprayed on a carbon cloth. The CCAs were reported to perform better in terms of power generation and COD removal because of their higher proton transfer rate, establishing CCA as a cost-effective option for scaling up of MFCs. Composite membranes consisting of polyvinyl alcohol (PVA), silicotungstic acid (STA), and graphene oxide (GO) were prepared and evaluated as proton-conducting membranes in air-cathode MFCs. These synthesized PVA-STA-GO membranes showed excellent kinetic properties, better durability, reduced oxygen crossover and higher power density compared to the commercially available Nafion 117 (Khilari et al., 2013b).

Ajayi and Weigele (2012) prepared a low cost membrane electrode assembly by coating a terracottapot with graphite paint and obtained a maximum power density of 33.13 mW/m² using a graphite felt anode. Efforts are being made over the past few years to prepare a sustainable low cost wastewater treatment system using baked earthenware as separators (Behera et al., 2010a; Behera et al., 2010b; Jana et al., 2010). This material is quite effective for proton transfer and has been used successfully as a low cost substitute to costly proton exchange membranes like Nafion, Ultrex, etc. It provides for better wastewater treatment and higher electricity generation than expensive proton exchange membrane materials (Jana et al., 2010). The cost of this earthenware membrane is 100 fold less than that of Nafion.

5. Membrane fouling

Membrane fouling is a problem in almost all membrane processes, which needs an immediate solution. The common fouling types are organic, colloidal, biofouling and scaling (Vermaas et al., 2012). Although performance of fouled membrane in other membrane processes can be partially restored by appropriate cleaning method, it will cause operational difficulties in MFCs and also add to the overall cost of the system (Ang et al., 2006; Creber et al., 2010; Kang and Cao, 2012). The major factors that affect membrane fouling are its physicochemical properties like water affinity, surface roughness, and electrostatic charge (Kang and Cao, 2012; Louie et al., 2006). Fouling of membrane or more specifically cathode fouling in single chamber MFCs reduces overall power output by reducing the exposed cathode surface area and by reducing oxygen diffusion to the active catalytic sites. Fouling of cathode also increases the resistance of the system (Vermaas et al., 2012). Fouling might also cause limitations in cation transfer thereby leading to losses in cathodic potential (Rikame et al., 2012). Xu et al., (2012) observed a 32.3% decrease in power production in MFC due to fouling of the membrane. Therefore, solutions are sought to inhibit fouling and also for removing fouling.

Surface modifications by changing the water affinity of the surface could be a possible option to reduce fouling. Researchers have said that hydrophilic membranes containing hydroxyl, carboxyl or ethylene oxide groups are better fouling resistant because most of the potential fouling compounds are hydrophobic in nature and a thin water layer on the membrane surface prevents hydrophobic foulants from getting attached to the membrane surface (Kang and Cao, 2012; Liu et al., 2012; Rana and Matsuura, 2010; Vermaas et al., 2012). However, for hydrophilic foulants membrane hydrophilicity will even increase fouling further (Kwon et al., 2005). Chen et al., (2012) prepared an air-cathode microbial fuel cell using hydrophilic polyvinyl alcohol (PVA) as binder and reported better coulombic efficiency (94%) and power density (1220 mW/m^2) of the MFC compared to the one prepared using glass fiber separator because of better fouling mitigation properties of PVA.

Another antifouling mechanism is to decrease the surface roughness of the membrane because fouling particles are more likely to be attached to rough surfaces than to smooth ones (Elimelech et al., 1997; Sagle et al., 2009; Vermaas et al., 2012; Vrijenhoek et al., 2001). The surface charge of the membrane is also an important factor in controlling fouling, as electrostatic repulsion between the membrane surface and the foulants will reduce membrane fouling (Vermaas et al., 2012). In an experiment on electrodialysis Vermaas et al., (2012) observed remnants of diatoms, clay minerals and organic fouling at the anion exchange membrane and scaling of calcium phosphate at the cation exchange membrane. However, the membranes will show distinct tendencies of fouling depending on the nature of the foulant. Once the electrical charge of the foulant is known this phenomenon can be easily used to reduce fouling. On a neutral surface deposition of foulants is less due to elimination of charge interaction between the membrane and foulants. Also steric repulsion due to presence of some surface-bound longchain hydrophilic molecule (like polyethylene glycol etc.) prevents attachment of larger molecules of foulants (Mcpherson et al., 1998; Nie et al., 2004; Vermaas et al., 2012; Wang et al., 2002; Wang et al., 2010).

Applying anionic or cationic surfactants at suitable concentrations on hydrophobic surfaces not only reduces bacterial attachment to the surface but also removes previously attached bacteria on the surface (Akuzov et al., 2013; Vermaas et al., 2012). However, when tested on hydrophilic surfaces the non-ionic surfactants showed no inhibition, showing that the reduction of biofouling is not only due to the toxicity of the surfactants but because of some hydrophobic interaction between the membrane surface and microbial cell. Vanillin (4-hydroxy-3methoxybenzaldehyde), a well-known food flavoring agent, could be used as a potential compound that reduces the biofilm formation on reverse osmosis (RO) membranes (Ponnusamy et al., 2010). It is reported that after adding Vanillin the biofilm

formation was inhibited up to 46.3% on polystyrene surface. Vanillin was also found to be effective in inhibition of biofouling in MFC as reported by Chatterjee and Ghangrekar (2013). A mixture of PVA and Vanillin was used as binder in a single chamber air-cathode MFC, which demonstrated only 8% decrease in power production as compared to 56% decrease for the MFC using only PVA, after five weeks of operation. Titanium dioxide (TiO₂) being a well-known photocatalytic agent and having a hydrophilic behavior, use of nano TiO₂ particles as anti-fouling agent is reported in literature (Akuzov et al., 2013). Other inorganic materials like silicon dioxide (SiO₂), Zeolite, silver nanoparticles and even mesoporous materials improves membrane resistance to fouling when coated on membrane surface (Kang and Cao, 2012). Oxidative processes are important for the cross-linking of the adhesive proteins secreted by microorganisms to adhere to any surface and inhibition of the oxidative processes could result in low cohesion strength of the protein adhesive films of microorganisms. Several antioxidants like gallic acid, ascorbic acid, tannic acid can reduce fouling by inhibiting their attachment to the surface (Akuzov et al., 2013), but the feasibility of using all these agents are yet to be tested on cathodes of MFC.

Today most researches on reducing membrane fouling are based on introduction of a hydrophilic layer, the reduction of surface roughness, improvement of charge property, and utilization of steric repulsion effect and use of biocides (Kang and Cao, 2012). The easiest way to obtain all these modifications of membrane surface is by surface coating. The modifiers used might only be connected to the membrane surface by van der Waals force of attraction, hydrogen bonding or electrostatic interaction, hence the antifouling properties of the modified membrane may be gradually lost due to loss or leaching of coating after long term use (Kang and Cao, 2012). Certain chemical processes can also be used to attain surface modification like using hydrophilizing treatment by certain acids (Kulkarni et al., 1996), radical grafting (Belfer et al., 2004), chemical coupling (Van Wagner et al., 2011), plasma polymerization (Zou et al., 2011), vapor deposition (Yang et al., 2011) etc. Winfield et al. (2013) used natural rubber as membrane and reported reduced fouling even after operation for one year.

Researchers have obtained contradictive results in terms of antifouling properties of hydrophilic and hydrophobic surfaces. While some claim hydrophilic surfaces are better fouling resistive, others claim the opposite. Foulants can be inorganic or organic, while inorganic fouling is resisted by hydrophilic surfaces and it enhances biofouling, providing a suitable surface for biotic organisms to grow. The major research papers on fouling resistance are dealing with water treatment and not with wastewater treatment. The properties of foulants in water and wastewater are different. While inorganic materials have to be majorly dealt with while treating drinking water, the major culprit in membrane based wastewater treatment technologies is biological growth. Hydrophobic surfaces by their water resisting properties do not support biological growth; however, they are not effective in reducing deposition of inorganic foulants. Using a biocide on a hydrophilic surface seems to be the solution to resist inorganic fouling as well as biofouling.

6. Challenges

The main barrier to wide-scale implementation of MFC technology is the issue with scaling it up for real implementation in field; hence it is necessary to develop cost-effective materials for fabrication of the MFC cathode. With increase in the anodic chamber volume requiring higher surface area of the electrode, the conductive resistance of normal carbon electrode increases resulting in higher ohmic losses. To avoid this, metal current collectors on the surface of the cathode are often used, as mentioned earlier. More efficient design of current collector is necessary to ensure proper contact between the cathode material and the current collector so that no losses could occur. Any loose contact or gaps between the collector and the cathode will lead to current loss, which will affect the power generated from the MFC.

The performance of gas diffusion layers also needs further investigation. The materials generally used for diffusion layer are hydrophobic, which renders it non-conductive. This hampers the overall performance of the MFC. Hydrophobic materials with some polar functional groups could be a good choice for diffusion layer material. Its hydrophobic nature will serve the purpose of reducing electrolyte loss and simultaneously the presence of polar groups will ensure better conductivity of the cathode surface.

Rozendal et al., (2008) estimated the cost of different materials used in laboratory scale MFCs and reported that cathode materials in air-cathode MFCs account for 47% of the total cost of the MFC. Pant et al., (2011) did an economic analysis of several bioelectrochemical systems and observed that the major components contributing to high cost of these systems are aeration equipment, costly catalysts, membranes and electrolyte buffers in decreasing order. To reduce the overall cost of MFC and make them commercially feasible and successful it is thus necessary to reduce the cost of materials used for cathode fabrication. This can be done by using cheaper catalysts (like copper pthalocyanin, iron pthalocyanin, co-tetramethyl phenyl porphyrin, cobalt oxide, nanoparticles, activated carbon powder), binders (PTFE, PVDF, PDMS) and conductive materials (modified carbon powder, polypyrroles).

As mentioned earlier the challenge lies in scaling up of MFCs. The maximum voltage that can be obtained in a MFC is 1.1 V using acetate as substrate in anode and oxygen as the cathodic electron acceptor (Logan, 2008). However, the voltage obtained from a MFC is always less than this maximum predicted voltage owing to several losses namely activation polarization losses, concentration polarization losses and ohmic losses (Du et al., 2007; Logan, 2008). Since the maximum voltage that can be obtained from a MFC is limited, hence to maintain similar Coulombic efficiency (around 30% say) as a laboratory scale MFC, it is necessary to maximize current produced in the scaled up MFC. To achieve this, suitable selection of electrode materials and configuration is necessary to optimize current density, and to minimize the losses that occur at higher current densities, that is concentration polarization and mass transfer losses. Maximum current generation depends on the maximum rate at which bacteria can oxidize a substrate and transfer electrons to the anode, which in turn depends on availability of substrate to bacteria present in biofilm. Thus, there are two limitations to current generation: bacterial kinetic limitation and substrate limitation. Kinetic limitation comes into play when the rate of electron uptake by the electrodes surpasses the rate of generation of electrons by bacteria. Electron generation by bacteria depends on biofilm mass, substrate utilization rate of electrogenic bacteria, and their growth rate and substrate availability. Biofilm mass can be increased by increasing anode surface area; however there is a limitation to maximum surface area that can be used for a particular substrate concentration otherwise substrate availability will be the rate limiting step. The maximum value of ratio of electrode surface area by volume of reactor is yet to be determined and depends on a number of factors like electrode material, reactor configuration, etc. Thus by achieving the optimum surface area by volume ratio substrate limitation and kinetic limitations can be surpassed. Hence, by reducing the mass transfer losses a scaled up MFC with higher current generation capability can be aimed for.

To scale-up a MFC instead of using a single large unit several small units can be connected together rather than increasing the size of a single MFC (Ieropoulos et al., 2008) in order to avoid increasing electrical resistance with size (Oliveira et al., 2013b). When the MFC units are connected in stacks then the total MFC size can be easily altered just by adding or removing individual units, thus adding up or reducing the power output respectively of the MFC. Despite of the advantages associated with stacking of MFCs, it results in problems like voltage reversal etc. Also, it has been observed that the MFC performs better when the stacks have their individual feed and electrical connections. This can again be a challenging task in the field. Several studies on MFC scale up prove that it is feasible but it is important to improve MFC design in order to achieve a marketable cell. Aelterman et al., (2006) in a study investigated the influence of the electrical circuit (series or parallel) on the power, voltage and current output of MFCs and observed that stacked MFCs did not deliver higher power densities than the individual MFCs. Yet, they created the possibility to produce an averaged power at more practical voltages and currents.

7. Conclusions

Air cathode MFC offers distinctive advantage by reducing overall footprint required and eliminating limitations of oxygen availability. A large number of materials have been explored for its utility in aircathode, with optimum design for commercial application yet to be achieved. Performance of air cathode MFC varies with configuration and type of materials used. Modification of cathode surface by changing its water affinity, charge, surface roughness, etc. can lead to a solution to the problem of fouling currently being faced.

Further studies on current collectors, conductive materials, diffusion layer materials, catalysts, binders and fouling resistant economic materials are required to improve cathode performance with long term stability, and make MFC competitive with the already established wastewater treatment technologies.

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