Jurnal Kejuruteraan 32(1) 2020: 51-59
https://doi.org/10.17576/jkukm-2020-32(1)-07

Aryl Diazonium Modification on Graphite Electrode in Microbial Fuel Cell: A Review

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Received 19 July 2019, Received in revised form 27 September 2019
Accepted 30 October 2019, Available online 28 February 2020

ABSTRACT

Usage of graphite electrode in a microbial fuel cell (MFC) is favored due to their electron conductivity and stability as a base material for the electrode. Also, graphite is favored as it allows the growth of biofilm, which can enhance the cell's performance. The efficiency is reported improved through modification. Aryl diazonium modification has been reported to induce biofilm formation on the electrode faster. The modification can be done spontaneously or through electrografting of aryl diazonium salt onto the electrode surface. Control over the quantity of grafted aryl diazonium is essential. A thick layer will cause the performance of the system to drop, which may impede the electron transfer from biofilm to the electrode. Aryl diazonium is preferred as it allows a robust biofilm formation when used as a surface modification on the graphite electrode. Modification using aryl diazonium allows the electrode to be more accommodative for biofilm growth, which will increase the performance of the system. However, it does not act as a redox mediator for the system. It has been reported that power density obtained using aryl diazonium modified electrode is 250 mW.m^{-2}, higher than unmodified graphite electrode of 125 mW.m^{-2}. However, not all bacterial species is compatible with aryl diazonium modification. The unmodified graphite biocathode allows a higher power density compared to aryl diazonium modified biocathode. Hence, depending on the quality of aryl diazonium modification and the types of inoculum used, MFC performance can be further maximized.

Keywords: Aryl diazonium; graphite electrode; microbial fuel cell; electrode modification

ABSTRAK

Penggunaan elektrod grafit di dalam sel fuel mikrob (MFC) telah dikaji dengan lebih lanjut. Antara sebab grafit menjadi pilihan sebagai elektrod adalah kerana ia berupaya mengalirkan elektron serta mempunyai kestabilan yang tinggi. Terdapat pelbagai bentuk elektrod grafit yang diguna pakai seperti berus, butiran dan felt. Perbezaan dari segi bentuk mempengaruhi luas kawasan permukaan untuk tindak balas berlaku. Grafit juga membenarkan perlekatan dan pertumbuhan biofilem sekaligus meningkatkan prestasi sel. Telah dilaporkan bahawa kecekapan dapat dipertingkatklan melalui modifikasi, antaranya dengan cara menggunakan aril diazonium. Modifikasi ini dilakukan melalui kaedah spontan atau melalui elektrocantuman garam aril diazonium pada permukaan elektrod. Kawalan keatas kuantiti cantuman aril diazonium adalah penting kerana ketebalan menpengaruhi prestasi sistem sekaligus menghalang elektron berpindah dari biofilem ke elektrod. Sifat aril diazonium adalah menggalakkan pertumbuhan biofilem, tanpa bertindak sebagai perantara redoks untuk sistem. Terdapat kajian menyatakan bahawa ketumpatan kuasa yang terhasil apabila menggunakan elektod terubahsuai aril diazonium adalah sebanyak 250 mW.m^{-2}, lebih tinggi daripada elektrod tidak terubahsuai (125 mW.m^{-2}). Walaubagaimanapun, bukan semua spesis bakteria sesuai dengan modifikasi aril diazonium. Ketumpatan kuasa yang diperoleh apabila menggunakan biokatod tidak terubahsuai adalah lebih tinggi berbanding biokatod terubahsuai aril diazonium. Oleh itu, prestasi MFC boleh dipertingkatkan lagi bergantung kepada faktor kualiti modifikasi aril diazonium dan jenis inokulum yang digunakan.

Kata kunci: Aril Diazonium; Elektrod Grafit; Sel Fuel Mikrob; Modifikasi Electrode

INTRODUCTION

Conventional energy sources such as fossil fuels are depleting fast due to high consumer demand. Fossil fuels must undergo combustion to produce energy, which leads to the production of carbon dioxide and other harmful pollutants. Therefore, this whole process of producing energy is not clean and green. Hence, there is a need to search for a new alternative source of energy generation, which is both cheap and eco-friendly. Microbial fuel cell (MFC) is a renewable, eco-friendly green technology, and capable of converting waste into energy (Tee et al. 2017).

The MFC combines biological catalytic activity, where the biological organisms are responsible for catalyzing electrochemical reactions, with abiotic electrochemical reaction and physics (Logan and Rabaey 2012; Logan and Elimelech 2012). This technology incorporates waste material, which is more favourable in terms of cost (Logan and Rabaey, 2012), as its fuel. The cost further reduced as it requires no need for precious metals (Morozan et al. 2011). Potter (1911) was the first to propose the concept of MFC, where *Saccharomyces cerevisiae* demonstrated the ability to produce electricity from glucose.

Today, there are many types and designs of MFC such as from the more basic form of the soil-based microbial fuel cell (Saleh et al. 2019) to the much more complicated microbial electrolysis cell (Shamsuddin et al. 2018) and so forth. However, the essential components across the different designs remain the same (Jana et al. 2010; Pant et al. 2010; Xafenias et al. 2015). As with many other advancing technologies, MFC is not without its own set of problem. Two of the most significant aims in MFC are to produce energy while treating the wastewater used as its fuel. As of now, low power production remains one of the biggest hurdles to the progress of MFC technology. Various studies are continuously being done to increase MFC performance, especially in electricity generation. Tee et al. (2016) reported a maximum power density of 55 $mW.m^{-3}$ from a tubular up-flow earthen pot MFC with air cathode, while Jana et al. (2010) reported 10.04 $W.m^{-3}$ obtained when utilising commercial proton exchange membrane in an up-flow MFC. Past researches reported on trying a variety of different wastewater in their MFC to find the highest power production and waste treatment achievable (Pant et al. 2010). It was reported that MFC could reduce heavy metal such as hexavalent chromium in wastewater from 10 $mg.L^{-1}$ to 0.3 ± 0.3 $mg.L^{-1}$ (97 % reduction) in the first 45 hours of operation at pH of 8 (Xafenias et al. 2015).

While in another report by Gangadharan and Nambi (2015), 100 $mg.L^{-1}$ hexavalent chromium was removed entirely (99.87 % is recovered via precipitation on the cathode) in the first 48 hours of operation while simultaneously producing a maximum power density of 767.01 $mW.m^{-2}$ (2.08 $mA.m^{-2}$). Besides fuel, MFC is dependent on its electrodes. Compared to the chemical fuel cell, an MFC's anode electrode must be able to allow the microorganism to adhere to it. While some cathode remains abiotic such as air cathode MFC (Park et al. 2017), some studies were done on the biotic cathode (Arana & Gude 2018; Rago et al. 2018; Rothballer et al. 2015; Rusli, Bakar, Loh, et al. 2018). Baudler et al. (2015) demonstrated the usage of metals such as copper and silver as MFC electrodes, did not inhibit the growth of biofilm. The previous review points out that stainless steel is also an excellent material for electrode, albeit not as good as copper but without the increased risk of corrosion, especially as the cathode (Wang et al. 2017). Apart from metals, several studies showed that graphite is a suitable material for anode (Wu et al. 2017; Tang et al. 2015). An extensive review on biocathodes of stainless steel and carbon-based draws the attention to the critical aspect of large surface area and high porosity to induce bacterial adhesion (Liu et al. 2013). Graphite electrode modification has been studied before by Ouis and Kameche (2017) to improve the bacterial longevity and enhancing electron transfer through graphite rod modification with pyrrole. Their study reported an increase of power density from 7 $mW.m^{-2}$ up to 25 $mW.m^{-2}$ when the electrode was modified.

GRAPHITE ELECTRODES FOR MICROBIAL FUEL CELL

An electrode is an essential component of an MFC, where oxidation and reduction reaction occurs. Therefore, an electrode must be conductive, has a large surface area, low resistivity, and resistant to corrosion (Madhavan et al. 2017). For instance, graphite fiber brush has the above characteristics, including porosity, is inexpensive and easy to fabricate, is capable of generating higher power production when compared to other forms of graphite electrode (Liu et al. 2013). According to Gong et al., carbon-based material such as graphite is suitable for use as the anode in MFC owing to their excellent chemical stability and electron conductivity (Gong et al. 2014). According to a study by Erable et al. (2017), the presence of bacterial community largely depends on the material used as an electrode, which therefore creates a cathodic biofilm on stainless steel and anodic biofilm on graphite. Since then, several studies have been done on graphite to understand its ability as a suitable electrode. Table 1 shows the list of studies done on the graphite electrode.

Formation of biofilm either on the anode or cathode has the potential to increase the MFC performance. For instance, stainless steel based material as a cathode in MFC has been reported to be compatible with *Geobacter sulfurreducens* (Soussan et al. 2013), and other marine originated biofilm to reduce fumarate or oxygen, which act as the electron acceptor. The ability of a microorganism to benefit MFC when becoming biofilm on the anode and cathode implies in the presence of electroactive reversible biofilm (Blanchet et al. 2015; Cheng et al. 2010; Strik et al. 2010). Therefore, there exists a need to find a suitable material for both electrodes and modification techniques to induce the growth of the electroactive reversible biofilm.

According to Tang et al. (2014), the addition of mediators to MFC has been used to enhance the performance of MFC. The soluble mediators can transfer electrons from non-electroactive microorganism to the anode. However, Yu et al. (2015) expressed the concerns on usage of harmful chemical mediators, which may cause pollution and higher cost, suggesting a need for environmentally friendly, quick and low-cost modification method. To solve the issue of losing mediators in the system, electrode modification with electroactive mediators can increase the MFC performance. The effect of the modification can reduce the large overpotentials of the electrodes (Bakar et

al. 2017a). Additionally, the distance between anode and cathode can also be a decisive factor in power production (Srikanth and Venkata Mohan, 2012).

MODIFICATION ON ANODE

An anode needs to be conducive towards anodic bacterial growth as its growth directly affects the performance of the system. Various strategies developed to improve MFC anode via modification of metal (Cheng et al. 2006) and nonmetals (Liu et al. 2005). According to Tang et al. (2014), electron transfer to the anode from bacteria can be enhanced by fixing mediators onto the surface of the anode. In a study by Yong et al. (2014), microbes formed a composite biofilm with graphene, which increases the performance output compared to the unmodified electrodes. Tang et al. (2015) reported an attempt of modifying a graphite anode by forming a layer of graphene on it, in an MFC. They succeeded in forming macropores through graphene, which in result produces a maximum power density of 0.67 ± 0.034 W.m^{-2}, which is 1.72 times higher compared to unmodified graphite plate. This result shows that there exists a possibility of increasing the power output of MFC through modification of the electrode. Picot et al. (2011) reported that the maximum power output of MFC from an unmodified anode was up to 50 ± 6 mW.m^{-2}, increased by two times (90 mW.m^{-2}) when the anode modified with aryl diazonium at a charge of 28 mC.cm^{-2}. The modification will change the surface properties of the electrode, causes a favorable interaction between negatively charge external environment of bacteria and positively charged anode surface. The improved chemical compatibility between the bacteria and the modification done on the anode, resulting in efficient electroactive bacteria biofilm, consequently increases the performance of MFC. Different electrode designed over the years, with the purpose to increase the surface area for biofilm formation as the quantity of biofilm correlates directly to system performance (Table 1). Figure 1 shows the necessary steps of biofilm formation, which is a recurring process when the dispersed sloughed-off cells reattach themselves onto surfaces. A lot of the modification

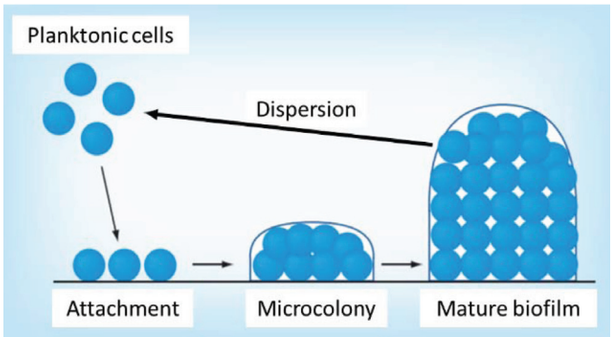

FIGURE 1. The basic flow of biofilm formation from single cells. Adapted from (Rabin et al. 2015)

involves direct modification of the anode surface to allow a more robust growth of bacteria. From the list, Tang et al. (2014) reported an increase of power density almost two times higher, from 967 ± 33 mW.m^{-2} to 1872 ± 42 mW.m^{-2}, when the graphite anode modified by using aryl diazonium cations. This result suggests that aryl diazonium may be suitable for bioanode formation.

MODIFICATION ON CATHODE

The condition of the cathode will affect MFC performance. An et al. relates the decrease in performance of activated charcoal carbon cathode linked to salt precipitation which causes the localized pH to increase from chemical precipitation (An et al. 2016). Erable et al. (2017) explained microbial biofilm on anodes tends to switch from their initial oxidative electroactivity being reductive when there is a lack of reducers and abundant of alternative oxidant. To these microorganisms, the oxidation reaction is much more desirable when there is both reducer and oxidizer present because of the ratio of synthetically provided reducers to oxygen (at pH of 7.0 and 20 °C) is 60:1. This ratio tells us that under a circumstance where oxygen and reducer are in excess in the cathode chamber or region, a reduction current will still occur albeit in a minimal amount compared to the oxidation current. Theoretically, in a 'reversible electrode' system where the reduction current from the cathode is equal to the oxidation current, oxidation of reducer at cathode should be 60 times higher than oxidation of oxygen (reduction current). In marine sediment, the ratio of oxidants and reducer are comparative due to the variety of electron sources and an abundance of electron acceptors. Therefore, the biofilm formation on a graphite-based electrode may be directed to be either more reductive or oxidative depending on the subject of study. Rothballer et al. (2015) had reviewed past studies and found that biocathode's microorganisms that were capable of reducing oxygen had been isolated. However, the catalytic ability and the biofilm were of poor quality; hence does not allow for an excellent performance. There are not many studies using graphite as a cathode when compared to the number of studies using graphite as the anode (Table 1).

ARYL DIAZONIUM MODIFICATION ON MICROBIAL FUEL CELL ELECTRODES

Aryl diazonium modification allows the formation of covalent carbon bonds (Ryder et al. 2016). The advantage of aryl diazonium salt is that it can easily grafted via electrochemical and chemical reduction process onto various types of surface such as carbon and polymer, thus proving their versatility (Raicopol et al. 2014; Raicopol et al. 2012). It was first reported by Delamar et al. (1992) who demonstrated chemiabsorption of aryl diazonium salt on glassy carbon surface by reduction, producing covalently attached layers.

TABLE 1. Some of the previous studies using graphite as either anode or cathode with their modifications and performances

Carbon type	Position (Anode inoculum)	Biocatalyst / modification	Substrate	Power production	COD reduction	Reference
Carbon felt	Anode (Mixed anaerobic sludge)	Graphene oxide and graphene oxide-zeolite	Acetate based feed	280.5 ± 14.4 $mW.m^{-2}$	80 %	Paul et al. (2017)
Graphite electrode	Anode (Marine sediments)	na[1]	Marine sediments + seawater + acetate	47 $mW.m^{-2}$	na[1]	Erable et al. (2017)
	The cathode (Anaerobic activated sludge)	Natural wolframite	Glucose based feed	135.57 $mW.m^{-2}$	na[1]	Shi et al. (2018)
	Anode (domestic wastewater)	Aryl diazonium	Acetate based feed	90 $mW.m^{-2}$	na[1]	Picot et al. (2011)
Graphite felt	Anode (mixture of anaerobic sludge and aerobic sludge)	electrodeposition of pyrrole	Glucose based feed	320 $mW.m^{-2}$	na[1]	Huang et al. (2016)
	Anode (*Shewanella putrefaciens*)	Polyaniline	No feeding	257 $mW.m^{-2}$	na[1]	Cui et al. (2015)
	Cathode (anaerobic digester sludge)	Multi-walled carbon nanotubes (MWCNTs) and oxidative acid pretreated MWCNTs	Glucose based feed	0.192 ± 4 $mW.m^{-2}$	na[1]	Wu et al. (2017)
	Anode (previously run MFC)	Reduction of anthraquinone-2-sulfonic acid diazonium cations	Acetate based feed	1872 ± 42 $mW.m^{-2}$	na[1]	Tang et al. (2014)
	Anode (Palm oil mill effluent) and carbon cloth cathode	poly(3,4- ethylenedioxythiophene	Acetate based feed	1620 $mW.m^{-2}$	86.30 %	Kang et al. (2017)
Graphite fiber brush	Anode (Fruit and vegetable residues)	na[1]	Fruit and vegetable residues or varying water-to-solid ratio and pre-digested organic matter	55 $mW.m^{-2}$	45 %	Jannelli et al. (2016)
	Anode (Fresh mud)	Aryl diazonium	Acetate based feed	0.82 $mW.m^{-2}$	na[1]	Rusli et al. (2018)
	Anode (previously run MFC)	na[1]	Acetate based feed	1651 ± 63 $mW.m^{-2}$	na[1]	Liu et al. (2013)
	Cathode (Wastewater)	na[1]	Wastewater	879 ± 16 $mW.m^{-2}$	na[1]	Chen et al. (2018)
Graphite plates	Anode (previously run MFC)	Exfoliated graphene and chemically reduced graphene powder	Acetate based feed	0.67 ± 34 $mW.m^{-2}$	na[1]	Tang et al. (2015)
	Cathode (aerobic sludge)	4-nitro benzene diazonium and 4-decyl aryl diazonium	demineralized water (cathode)	na[1]	na[1]	(Rothballer et al. 2015)
Graphite composite	Cathode (municipal wastewater)	MnO2 and MoS2	Glucose based feed	114 $mW.m^{-2}$	na[1]	Jiang et al. (2017)
Graphite rod	Anode (Compost leachate)	Pyrrole by Electro-polymerisation	Compost leachate	25 $mW.m^{-2}$	na[1]	Ouis and Kameche (2017)
	Anode (previously run MFC)	Graphite rods array	Acetate based feed	na[1]	na[1]	Li et al. (2017)
	Anode (previously run MFC)	Carboxylate and sulfonamide via reduction of aryl diazonium	Acetate based feed	118 $mW.m^{-2}$	na[1]	Commault et al. (2015a)
	Anode (Soil)	Carboxyl group via reduction of aryl diazonium	Acetate based feed	100 ± 19 $mW.m^{-2}$	61.50 %	Commault. al (2015b)
	Cathode (Palm oil mill effluent anaerobic sludge)	HNO3	Acetate based feed	36.438 $mW.m^{-2}$	33 %	Asghar et al. (2016)
	Cathode (Palm oil mill effluent anaerobic sludge)	Nitrogen doping	Acetate based feed	47610 $mW.m^{-3}$	98 %	Asghar et al. (2017)
	Cathode (Previously run MFC)	H3PO4, HNO3, ZnCl2, urea, melamine	Acetate based feed	790 $mW.m^{-2}$	na[1]	Zhang et al. (2016)
Pencil deposited graphite	Anode and cathode (Shewanella oneidensis MR-1 strain)	na[1]	Tryptic soy broth (No feeding, only for culturing)	5.68 $mW.m^{-2}$	na[1]	Lee et al. (2016)

Aryl diazonium salt is capable of introducing various functional groups into the aromatic ring through nucleophilic aromatic substitutions (Mahouche-Chergui et al. 2011). Figure 2 shows the chemical structure of aryl diazonium salt, especially the presence of the integral aromatic ring. Various materials such as epitaxial graphene (Bekyarova et al. 2009), nanocarbons (Jin et al. 2009), chemically converted graphene (Lomeda et al. 2008), mechanically exfoliated graphene (Lim et al. 2010) and chemical vapor deposit monolayer graphene (Eissa et al. 2014) have been functionalized with different aryl layers. Delamarche et al. (1994) reported that the formation of aryl diazonium composition structures is not natural to be controlled because the radicals formed are highly unselective. Ideas to address this issue had been demonstrated, such as by simultaneous electrografting and consecutive electrografting with one of the aryl component in excess (Jiang et al. 2016). Formation of aryl layers has been reported in immobilization of biological component such as whole-cell (Harper et al. 2009). The aryl layers formation is an essential key factor in the formation of biofilm and more so on bioelectrodes for MFC.

Ever since then, the interest in aryl diazonium has skyrocketed. This organic chemical compound has even been used to create biosensor electrodes in order to reduce interference when collecting data (Raicopol et al. 2016; Serafín et al. 2017). It was reported by Bakar et al. (2017b) that aryl diazonium modified electrode is electrochemically stable in an enzymatic fuel cell as a biosensor for lactose detection. Some of the most common ways to modify graphite electrode is first to create diazonium salt which then either reduced spontaneously or by electroreduction of the salt, controlled by the amount of cycle if used on potentiostat, or by being charged with external power source (Anam Asghar et al. 2016; Commault, L. et al. 2015; Picot et al. 2011; Rothballer et al. 2015; Rusli, Bakar, Rani, et al. 2018). In a report by Picot et al. (2011), the best-performed aryl diazonium modified electrodes are the one that electrografted by applying a charge of 28 $mC.cm^{-2}$ (produced power of more than 90 $mW.m^{-2}$).

In contrast, the worst-performing modified by applying 200 $mC.cm^{-2}$ (produced power less than 10 $mW.m^{-2}$). This result shows that not only the nature of grafted modification is essential, but the quantity of the applied modification is also necessary when performing a surface modification with aryl diazonium. In a report by Smida et al. (2018), diazopyridinium cations, which is another derivative of aryl diazonium, allow immobilization of thin and compact pyridine units, which led to a higher power production when implemented in acetate fed MFC. The thin and compact pyridine layer does not block the transfer of electron as well as being hydrophilic, thus allowing better attachment of microbes to the electrode. The modification improves the electrode surface environment to be more supportive for microbes to adhere and form a biofilm to grow. It was reported by Lapinsonni et al. (2013) that the modification of electrode with boronic acid, using aryl diazonium electrochemical reduction, generated a higher power density of almost 250 $mW.m^{-2}$ compared to the unmodified electrode. The boronic acid modification allows for better attachment of bacterial lipopolysaccharide to the modified electrode, thus resulting in better biofilm formation and also better performance.

The previous study reported that aryl diazonium electrode modification could enhance the performance of MFC (Tasca et al. 2011). The modification provides in better direct electron transfer, significantly higher than previously reported and produced higher stability in current production when compared to the unmodified electrode. Saito et al. (2011) observed that the lowest amount of modification led to the highest power production and increase of nitrogen content in diazonium modification can improve MFC performance. One of the causes of low power production in MFC is the low rate of extracellular electron transfer from bacteria to the anode, which can be further related to biofilm formation on the electrode. A relationship study of surface modifications on biocathode microbial biofilm population exhibited the unmodified was better than the modified (Rothballer et al. 2015). They assumed that the γ proteobacteria species involved in oxygen reduction reaction, might not find the condition created by the modification favorable for its growth since its population growth is very low. Table 2 tabulates the percentage of the said species on each electrode. Better performing unmodified biocathode covered dominantly with γ proteobacteria. The study can show that adherence of certain species of bacteria to aryl diazonium modified electrode may be affected by the type of aryl diazonium salt used to modify the electrode. In bioanode however, it was reported that Geobacter-dominated biofilm on carboxyl group grafted graphite rod through aryl diazonium modification maintained electrically active after six weeks of operation in synthetic wastewater, compared to other species introduced in the system (Commault, Lear, et al. 2015). This finding shows that aryl diazonium modification has a high affinity with Geobacter species and capable of allowing a stable biofilm formation on bioanode.

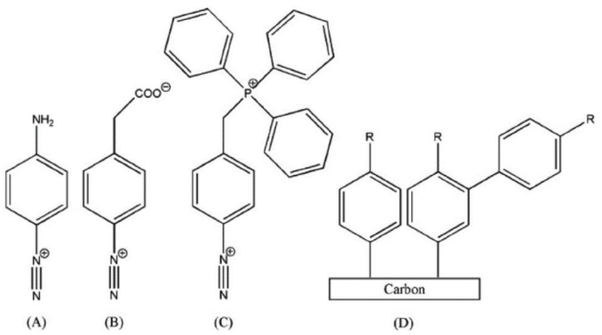

FIGURE 2. Chemical structure of aryl diazonium salt which contains aromatic rings. (A) 4-phenylamino diazonium, (B) 4-benzyltriphenylphosphonium diazonium, (C) 4-phenylacetic acid diazonium, (D) Scheme describing the nature of modified carbon surface, R=NH_2.CH_2COO^- or $CH_2PPh_3^+$. Adapted from (Picot et al. 2011)

TABLE 2. The percentage of biofilm species on the unmodified electrode and aryl diazonium modified electrode (N = 4-nitro benzene diazonium, D = 4 Decyl Aryl Diazonium) with different degree of modification (20 and 0.5 represents the number of applied cycles). Adapted from (Rothballer et al. 2015)

Phylum	Family	Inoc.[1]	Catholyte		Biofilm							
		%	N-20 %	D-20 %	unm[2] %	D-0.5 %	N-0.5 %	N-20 %	D-20 %	unm[2] %	D-0.5 %	N-0.5 %
Acidobacteria	*IncertaeSedis*	1.1	4.6	1.9	3.1	6.9	11.3	3.6	3.6	11.1	8.5	4.6
Actinobacteria	*Micrococcaceae*	0	1.3	0	0.8	8.6	3.2	0	0	0	0	0
Actinobacteria	*Nocardiaceae*	0	3.3	10.7	5.0	4.6	10.3	0.6	0.4	0	.3.2	2.0
Chloroflexi	*Anaerolineaceae*	3.4	0.9	0	4.4	0.7	24.6	0.5	0.4	8.6	0.3	6.8
Firmicutes	*Lachnospiraceae*	1.1	8.7	0	6.2	6.1	0	5.2	6.2	0.1	3.7	15.0
Firmicutes	*Ruminococcaceae*	0.4	8.4	0	3.6	4.4	0	4.4	4.2	0	2.6	8.7
Firmicutes	*Veillonellaceae*	0.4	8.7	0	8.0	5.4	0	6.3	7.6	0	4.2	16.3
Proteobacteria α	*Bradyrhizobiaceae*	0	0.3	4.4	0.6	1.7	0.7	0.2	0.3	0.3	1.9	0.6
Proteobacteria α	*InicertaeSedis*	0	1.3	0.3	1.0	0.9	0.7	0.6	0.6	0	0.2	1.5
Proteobacteria α	*Rhodobiaceae*	0.9	2.7	6.2	4.3	1.3	0.6	1.0	0	0	2.2	0.8
Proteobacteria β	*Alcaligenaceae*	6.4	0	0	0.3	0	0	0.4	0	0	0	0.7
Proteobacteria β	*Comamonadaceae*	41.0	20.5	52.4	13.7	21.9	16.4	7.9	5.9	1.9	24.6	5.3
Proteobacteria β	*Rhodocyclaceae*	10.7	10.5	5.3	11.1	11.3	3.6	9.1	10.4	2.5	10.1	9.0
Proteobacteria γ	*unclassified*	0.4	0	0.8	0	0.4	0	46.8	47.2	60.7	24.0	2.0
Proteobacteria γ	*Xanthomonadacea*	1.3	4.5	6.3	3.6	3.8	7.2	1.9	1.8	2.2	3.6	1.8
	Simpson (1-D)	0.90	0.95	0.89	0.96	0.96	0.88	0.75	0.74	0.57	0.90	0.96
	Shannon (H)	3.11	.3.48	2.65	3.47	3.69	2.64	2.44	2.35	1.49	3.02	3.68

[1]inoculum
[2]unmodified

CONCLUSION

Graphite has been widely used as an electrode in the MFC system, especially as an anode. The chemical stability and high electron conductivity inherent to this material make it a suitable material to be used as part of MFC technology. However, the studies that utilized graphite material as the anode are more than the cathode. Improvement on electrode has been accepted as a method that can be used to enhance the said inherent capabilities of graphite. One of the main advantages of modification is that it will create an environment suitable for a microbe to adhere and form a biofilm, which in result, directly increases the overall performance of MFC. One way of modification is by using aryl diazonium salt. Aryl diazonium salt can be modified either spontaneously or by electroreduction. Electroreduction of aryl diazonium using boronic acid allows for a better attachment of microbes to electrode due to its affinity with bacterial lipopolysaccharide. However, not all bacteria find aryl diazonium modified electrode to be suitable for their growth. Despite this, the usage of aryl diazonium modification is prevalent in the biosensor field due to its affinity with an organic compound. Because of this, it should be compatible for usage in the MFC system as the concept are not that different. Hence more study needs to be done to identify species that can work with aryl diazonium modified electrode synergistically to further maximize the capability of aryl diazonium modified electrode.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support given for this work by GGPM-2017-012 from Universiti Kebangsaan Malaysia (UKM).

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