Recent advances in the development and utilization of modern anode materials for high performance microbial fuel cells

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\textbf{A B S T R A C T}

Microbial fuel cells (MFCs) are novel bio-electrochemical device for spontaneous or single step conversion of biomass to electricity, based on the use of metabolic activity of bacteria. The design and use of MFCs has attracted considerable interests because of the potential new opportunities they offer for sustainable production of energy from biodegradable and reused waste materials. However, the associated slow microbial kinetics and costly construction materials has limited a much wider commercial use of the technology. In the past ten years, there has been significant new developments in MFCs which has resulted in several-fold increase in achievable power density. Yet, there is still considerable possibility for further improvement in performance and development of new cost effective materials. This paper comprehensively reviews recent advances in the construction and utilization of novel anodes for MFCs. In particular, it highlights some of the critical roles and functions of anodes in MFCs, strategies available for improving surface areas of anodes, dominant performance of stainless-steel based anode materials, and the emerging benefits of inclusion of nanomaterials. The review also demonstrates that some of the materials are very promising for large scale MFC applications and are likely to replace conventional anodes for the development of next generation MFC systems. The hurdles to the development of commercial MFC technology are also discussed. Furthermore, the future directions in the design and selection of materials for construction and utilization of MFC anodes are highlighted.

\section{1. Introduction}

The growth in the use of energy has a direct link with the well-being, quality of life and prosperity of a society. There is an increasing need for not only generating sufficient energy, but also to find energy from new sources that are safe, sustainable and environmentally friendly. As the availability of coal, oil and gas are being exhausted (Aziz et al., 2013), there is a growing need to consider alternate energy sources. A reliance on the current renewable energy sources alone will not sufficiently meet the required needs in the future. It would be increasingly necessary to rely on the discovery of new energy sources in order to continue to meet future energy needs (Sukhatme, 2011).

One of the promising solutions for addressing this energy problem is to develop and deploy specific energy sources for different utilities. This will involve developing strategies that enable derivation of energy from waste materials. For example, across the world, huge volumes of wastewater are continuously pumped directly into rivers, streams and the oceans. The impact of this huge wastewater disposal is severe, ranging from damage to the marine environment and to fisheries. Such disposal of wastewater does little to preserve water at a time when we are facing serious global water shortage and the problem is likely to be exacerbated with the impact of climate change. Yet, in many cases, the
effluent contains significant amount of organic substances which are potentially significant source of energy. One way of achieving this is by using microbial fuel cell (MFC) which is capable of directly converting chemical energy present in the organic materials to electricity by using microorganisms as catalysts (Thepsuparungsikul et al., 2012; Tsai et al., 2009; Zhao et al., 2010). The electricity generated can be used for maintenance and operation of the wastewater treatment facility, and, thus, creating a self-sustaining energy supply for the water treatment facility and, hence, to reduce operational costs (Liu et al., 2004).

A typical microbial fuel cell consists of an anode and a cathode compartments separated by proton exchange membrane, as illustrated in Fig. 1. The anode is the site where biocatalyst grows in the form of biofilm which promotes the decomposition of organic materials to produce electrons and protons. The electrons are transferred to the cathode compartment through an external circuit, while the protons are transferred to the cathode compartment through the proton exchange membrane (PEM). The electrons and protons are consumed in the cathode compartment with the protons combining with oxygen to form water (Min and Logan, 2004; Torres et al., 2010), as shown in Fig. 1. The chemical reactions which occur in the anodic and cathodic chambers, respectively, are given by Eqs. (1) and (2) below (Rahimnejad et al., 2015):

Anodic reaction - $\text{C}_2\text{H}_4\text{O}_2+2\text{H}_2\text{O} \rightarrow 2\text{CO}_2+8\text{H}^++8\text{e}^-$  

Cathodic reaction - $2\text{O}_2+8\text{H}^++8\text{e}^- \rightarrow 4\text{H}_2\text{O}$  

Fig. 1. Working principle and basic construction of MFC.

The chosen electrode materials play a significant role in the performance of the MFC and it is critically important for successful utilization of this technology for efficient energy generation. In past two decades, many different materials have been explored as anodes for MFCs. While most of the earlier studies focused on the use of carbon based material, such as graphite rod, graphite felt, carbon cloth, flexible graphite sheets, graphite granules and activated carbon (Li et al., 2010; ter Heijne et al., 2008; Wang et al., 2009; Wei et al., 2011), recent studies have found that these two dimensional electrode materials have many limitations, such as low surface area, high internal resistance, high activation and mass transfer over-potential which hinders their ability to achieve high performance with MFCs. With recent advances in materials science and nanotechnology, the use of second generation three-dimensional (3D) electrode material has attracted considerable interest for the development of MFCs. In 2007, Logan et al. (2007) developed a graphite fibre brush anode electrode with a 3D structure. They achieved a maximum power density of 2400 mW/m² with a single chamber air cathode. 3D surface anodes offer high surface areas for efficient colonization of bacterial communities and, hence, for increasing substrate access to the anode respiring bacteria (ARB) and, consequently, minimizing mass transfer limitation (Liu et al., 2010). In addition to this surface characteristics, 3D surface anodes are very quintessential in adhesion of bacterial colonies, have high volume to surface ratio, and good biocompatibility (Cui et al., 2015; Garcia-Gomez et al., 2015).

The anode surface also plays a significant role in promoting and maintaining bio-catalytic activity. Surfaces can be modified to become favourable habitats for biofilms which are capable of enhancing electron transfer from bacteria to anode surface. Generally, the achievement of more bacterial adhesion enables the generation of more power with minimum loss (Jiang and Li, 2009). It has been demonstrated in a recent study that surface modification not only increases MFC system performance, but also decreases the MFC startup time (Luo et al., 2013).

Many studies have also recently developed and extensively studied the use of graphene-based anodes, composite anodes, and surface modified anodes (Kumar et al., 2013). Each electrode material has its own merits and demerits. Metal based or metal composite anodes have not been thoroughly studied or explored for MFCs. Most of the metals failed to pass the set criteria for best anode electrodes for MFC because of their tendency to corrode (Wei et al., 2011). Poczaznoi et al. (2012) claimed recently that, of most metals, stainless steel is the most promising material for MFC anodes. However, there is still a lot of scope for further improvement in the use of stainless steel for MFC anode development, as well as other new low cost efficient materials (Poczaznoi et al., 2012).

The achievement of large scale development and economic viability of MFCs systems requires the availability of cost effective anodes capable of achieving higher performance for long term operation, while also involving easy maintenance or, where possible, to be completely free of maintenance (Chen et al., 2012b).

This paper reviews the recent advances in the development of anode materials and configurations over the past five years. The considerable developments in anode materials for microbial fuel cells within this period is illustrated in Fig. 2 and this clearly demonstrates that the
The choice of an anode material and its architecture can directly affect key performance parameters, such as microbial adhesion, electron transfer and fuel oxidation. The achievable power density of a MFC system is dependent on the choice of an anode which defines the power density limit and can significantly affect the performance of a MFC system (Xie et al., 2011). Consequently, the achievement of a higher power density requires a capacity to promote better electron transfer from the bacterial community to the external circuit, and the anode is central in achieving this goal (Torres et al., 2010). The mechanism of the electron transfer process necessitates the donation of electron from the anode respiring bacteria (ARB) to the anode surface via extracellular electron transfer (EET) and, consequently, resulting in the passage of a current in the external circuit. This current results from the uni- or bidirectional flow of electrons from the anode to the cathode. The current flow is driven by the electrochemical reactions proceeding sections.

2. Anode materials for MFCs

The choice of an anode material and its architecture can directly affect key performance parameters, such as microbial adhesion, electron transfer and fuel oxidation. The achievable power density of a MFC system is dependent on the choice of an anode which defines the power density limit and can significantly affect the performance of a MFC system (Xie et al., 2011). Consequently, the achievement of a higher power density requires a capacity to promote better electron transfer from the bacterial community to the external circuit, and the anode is central in achieving this goal (Torres et al., 2010). The mechanism of the electron transfer process necessitates the donation of electron from the anode respiring bacteria (ARB) to the anode surface via extracellular electron transfer (EET) and, consequently, resulting in the passage of a current in the external circuit. This current generation mechanism has been elucidated to be similar to direct electron transfer from cell to anode surface, diffusion of soluble electron shuttles and electron transfer through solid component (pili) from biofilm (Torres et al., 2010). Key properties for anode materials to achieve a high performance include biocompatibility (Rahimnejad et al., 2015; C.-T. Wang et al., 2013; Xie et al., 2011), corrosion resistant (Pocaznoi et al., 2012; Rahimnejad et al., 2015), low electrical resistance (Rahimnejad et al., 2015; Song et al., 2015) and high electrical conductivity (Rahimnejad et al., 2015). The anode must also be made of chemically stable material which is capable of working in environment which contains varied and diverse biodegradable wastewaters containing various organic and inorganic constituents capable of reacting with the anode material to cause deterioration and performance reduction (Shen et al., 2014).

In the last five years, a lot of anode materials have been used for the construction of anodes for MFC systems. In particular, the material of choice for anode construction is influenced significantly by advances in various system architectures of MFCs. Notably, the use of different non-conventional carbonaceous anode materials is on the rise. This new class of carbonaceous anodes includes stainless steel (Pocaznoi et al., 2012), surface modified stainless steel (Hou et al., 2015, 2014; Ledezma et al., 2015; Mosqud et al., 2013; Zhu and Logan, 2014) and graphene-based anodes (Chou et al., 2014; Xie et al., 2011; Yuan and He, 2015; Zhang et al., 2011). The graphene-based anodes are very promising and have been reported in several recent studies. The use of composite graphene anodes has also been reported to produce high power density (Chen et al., 2014; Gnanakumar et al., 2014; Hou et al., 2013; Qiao et al., 2014; H. Wang et al., 2013). Similarly, the use of single walled carbon nanotubes (Cui et al., 2015; Xie et al., 2011), multi-walled carbon nanotubes (Thepsuparungsikul et al., 2012), and carbon nanofibers anodes has also been reported (Shen et al., 2014) for high performance MFCs. Some of the recent advances in anode materials and configurations have been categorised in this review into four broad types, namely modern carbon-based anodes, metal-based anodes, carbon-based composite anodes, and surface modified metal-based anodes. Each of these categories is discussed separately in the proceeding sections.

2.1. Modern carbon-based anodes

In the past decade, several carbon-based materials have been proposed and demonstrated for use as anode in MFC systems. These include carbon paper, graphite plates or sheets, graphite rod, and carbon cloth (Wei et al., 2011). The advantages of using carbon-based anode materials include low cost, biocompatibility, excellent electrical conductivity and chemical stability (Wei et al., 2011). This group of materials have been acknowledged as being very useful for construction of MFCs because of their potentially high performance improvement and excellent properties. One of the important factors that influence the performance of these anode materials is the accessible surface area. The data provided in Table 1 demonstrate that several carbon based anodes offer very high accessible surface areas, up to 1018 cm² (Sonawane et al., 2014). The various types of modern carbon-based
anodes that have been used for MFCs are described in more details in the subsequent sub-sections.

2.1.1. Natural anode materials

The synthesis of high performance anode materials involving the use of natural and recyclable materials provides an excellent green approach for deriving useful energy from nature and also for ensuring sustainability (Chen et al., 2012b). Development of layered corrugated carbon (LCC) anode from inexpensive packaging material by carbonization is an interesting example. Fig. 4a shows a single recyclable LCC anode and the corresponding scanning electron micrograph of a bamboo charcoal tube surface is shown in Fig. 4b. It is important to note that the 3D surface of the LCC can usually be tuned by varying the layers and flute height. Increasing the number of layers from one to six resulted in a linear increment in current density due to the provision of increased surface area for biofilm. It has been demonstrated that LCC gives up to four-fold increase in current density when compared to conventional graphite felt (Chen et al., 2012b).

Natural anode materials are suitable low-cost alternatives for MFCs because of their meso/microporous 3D structures, high electron transfer rate and the achievable high kinetics of electroactive bacterial community (Karthikeyan et al., 2015). Majority of the recently developed highly porous 3D anode materials utilised natural material LCC as an inexpensive and high performance anode material, usually prepared from recycled paper by carbonization (Chen et al., 2012a, 2012b; Zhang, 2014; Karthikeyan et al., 2015).

High performances have also been achieved with 3D anodes based on the three-dimensional growth of exo-electrodes. A better anode kinetics can be accomplished by increasing the anode surface area, but the performance only improves when reaction occurs at the triple phase boundary i.e. anode, cathode and electrolyte with a lower internal resistance. To minimize the internal resistance of the system (Li et al. (2013) and Chen et al. (2011)) developed an anode from Kenaf (Hibiscus cannabinus) stem by using heat drying carbonization at 1000 °C under N2 environment. The resulting material was connected to stainless steel wire to make a complete anode electrode. Kenaf contains natural 3D structure in its stem so it offers mesoporous ordered structure for growth of biofilm and also the electrical conductivity is sufficient to consider it as a suitable electrode material. A piece of Kenaf of 10 mm diameter and 15 cm in length had only 10 Ω resistance. It also exhibits a power density three times higher than that of graphite under the same experimental conditions (Chen et al., 2012b; Li et al., 2013). It has also been reported that carbonized king mushroom, wild mushroom and corn stem exhibited good electrode properties (Chen et al., 2012a). Interestingly, carbonized corn stem exhibits 8 times better performance than plane graphite electrode. Fig. 5 shows some of the natural materials such as (a, b) king mushroom, (c, d) wild mushroom and (e, f) corn stem that have been used as anode materials for MFCs. The scanning electron micrographs of these materials indicates that they have high porosities and large surface areas/roughness (Karthikeyan et al., 2015). Similarly prepared bamboo charcoal has also been found to exhibit good electrode properties compared to a conventional graphite rod. The SEM image of a bamboo charcoal tube surface which was very rough with many visible cracks, was shown previously in Fig. 4b (Zhang, 2014). Nevertheless, some of the observed advantages of this electrode material include low internal resistance, better biocompatibility and rougher surface which promoted biofilm adhesion. It was obvious from the results obtained in a recent study (Zhang, 2014) that the introduction of C=N bonds facilitates electron transfer from bacteria to the anode. Consequently, the bamboo charcoal gave 50% better performance than a graphite tube (Zhang, 2014). Obviously, the kinetics and performance are improved substantially with the accessibility of high anode surface area to microbes.

The use of granular electrodes for MFCs provides a cost effective approach for creating high surface areas that are beneficial for achieving high current and power densities (Deeke et al., 2015). Activated carbon (AC) granules attached with exoelectrogens are capable of extracting electrons from acetate and storing the electrons in the granules (Deeke et al., 2015). This behaves like a capacitor where AC granules are charged in charging column and the stored charge is harvested from the AC granules in an external discharge cell. During charging of AC granules, cations surround the granules along with charge, making this charging mode form a double layered capacitor. Consequently, during discharge of AC granules, cations are also released along with the charge, resulting in a local high conductivity which leads to minimal ohmic losses. Also, mass transfer loss is minimized because of the well-mixed system architecture. In general, wastewater with low conductivity does not pose major limitations for use with charging AC granules (Deeke et al., 2015).

Granular activated carbon (GAC) fluidized (with stirring) in an anode chamber results in intermittent contact with GAC and the current collector. It has been demonstrated in a recent study that the maximum power densities produced with and without stirring are 951 mW/m² and 813 mW/m², respectively (Liu et al., 2014). Evidently, stirring has a beneficial effect in increasing the power density by 17% and the results confirmed that the biofilm produced on GAC behaves like a capacitor. The charge stored in the bacterial biofilm and GAC granules is discharged when in contact with the current collector (Liu et al., 2014).

A recent study (Peng et al., 2014) has also demonstrated that the capacitance behaviour of anode is significantly increased with the addition of Fe3O4. Chen et al. (2015) proposed a new approach for making an anode for MFC, based on the use of porous carbon with defined pore size. It was demonstrated that the achieved performance of the MFCs was four times better than obtained with the use of a pristine carbon felt anode.

Layered corrugated electrode, produced from the carbonization of one of the most abundant packing materials, was found to be the best performing anode among all carbon based anodes. The achieved
current densities were 200 A/m² and 390 A/m² from three and six corrugated layers, respectively (Chen et al., 2012b). This is the least expensive and high performance material for MFC construction.

### 2.1.2. Synthetic anode materials

It has been demonstrated that three-dimensional nonwoven carbon fibre prepared by electrospinning and solution blowing (Fig. 6a) can achieve a maximum current density up to 30 A m⁻² (Chen et al., 2011). The occurrence of inter-fibre junctions as crosslinking points are evident in Fig. 6a and these are important for providing additional improvement of performance. Fig. 6b–d shows the images of graphite rod, carbon fibre veil and graphite fibre brush anode before biofilm formation. A 3D interlaced carbon yarn anode in stainless steel frame with double sided air cathode developed by Sonawane et al. (2014) is shown in Fig. 6e. The performance of MFCs based on these 3D materials also depends upon the system architecture (Sonawane et al., 2014). Double sided air cathode helps to reduce mass transfer limitations. With this design, stainless steel frame has been used as a current collector and as a support for the carbon fibre veil and graphite rod prepared by electrospinning and solution blowing (Fig. 6a) can achieve a maximum current density up to 30 A m⁻² (Chen et al., 2011).

### Table 1

A brief account of carbon based anode materials explored in MFC research.

<table>
<thead>
<tr>
<th>Carbon based anode</th>
<th>Anode</th>
<th>Cathode</th>
<th>System architecture</th>
<th>Source of inoculation</th>
<th>Substrate</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered corrugated carbon</td>
<td>NA</td>
<td>Three-electrode cell</td>
<td>Primary wastewater</td>
<td>Artificial wastewater</td>
<td>26.52</td>
<td>390⁺</td>
<td>(Chen et al., 2012b)</td>
</tr>
<tr>
<td>3D carbon material</td>
<td>NA</td>
<td>Electrochemical cell</td>
<td>Domestic wastewater</td>
<td>Acetate substrate</td>
<td>5.11</td>
<td>25.3</td>
<td>(Chen et al., 2012b)</td>
</tr>
<tr>
<td>Three-dimensional carbon fibre</td>
<td>NA</td>
<td>Electrochemical cell</td>
<td>Wastewater</td>
<td>Artificial wastewater</td>
<td>NA</td>
<td>30</td>
<td>(Chen et al., 2012b)</td>
</tr>
<tr>
<td>Graphite rod</td>
<td>NA</td>
<td>Three-electrode half cell</td>
<td>Domestic wastewater</td>
<td>Artificial wastewater</td>
<td>11.5</td>
<td>5.17</td>
<td>(Lin et al., 2010)</td>
</tr>
<tr>
<td>Polycrystalline carbon rod</td>
<td>NA</td>
<td>Three-electrode half cell</td>
<td>Domestic wastewater</td>
<td>Artificial wastewater</td>
<td>15</td>
<td>4.96</td>
<td>(Lin et al., 2010)</td>
</tr>
<tr>
<td>Carbon fibre veil</td>
<td>NA</td>
<td>Three-electrode half cell</td>
<td>Domestic wastewater</td>
<td>Artificial wastewater</td>
<td>12</td>
<td>7.05</td>
<td>(Lin et al., 2010)</td>
</tr>
<tr>
<td>Graphite foil</td>
<td>NA</td>
<td>Three-electrode half cell</td>
<td>Domestic wastewater</td>
<td>Artificial wastewater</td>
<td>15</td>
<td>0.07</td>
<td>(Lin et al., 2010)</td>
</tr>
<tr>
<td>Polycrystalline carbon rod</td>
<td>NA</td>
<td>Three-electrode half cell</td>
<td>Domestic wastewater</td>
<td>Artificial wastewater</td>
<td>15</td>
<td>9.21</td>
<td>(Lin et al., 2010)</td>
</tr>
<tr>
<td>Glassy carbon rod</td>
<td>NA</td>
<td>Three-electrode half cell</td>
<td>Domestic wastewater</td>
<td>Artificial wastewater</td>
<td>3.18</td>
<td>2.5</td>
<td>(Lin et al., 2010)</td>
</tr>
<tr>
<td>Carbon paper</td>
<td>NA</td>
<td>Three-electrode half cell</td>
<td>Domestic wastewater</td>
<td>Artificial wastewater</td>
<td>7</td>
<td>12.58</td>
<td>(Lin et al., 2010)</td>
</tr>
<tr>
<td>Interlacing carbon yarn</td>
<td>Air cathode</td>
<td>Single chamber dual cathode</td>
<td>Distillery wastewater</td>
<td>Distillery wastewater</td>
<td>1018</td>
<td>18.15</td>
<td>364</td>
</tr>
<tr>
<td>Interlacing carbon yarn</td>
<td>Air cathode</td>
<td>Single chamber dual cathode</td>
<td>Domestic WW</td>
<td>Domestic WW</td>
<td>1018</td>
<td>22.04</td>
<td>621</td>
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<tr>
<td>King mushroom carbon</td>
<td>NA</td>
<td>Mini glassy bioreactors</td>
<td>Sewage treatment plant</td>
<td>Acetate media</td>
<td>0.25</td>
<td>20.9</td>
<td>NA</td>
</tr>
<tr>
<td>Wild mushroom carbon</td>
<td>NA</td>
<td>Mini glassy bioreactors</td>
<td>Sewage treatment plant</td>
<td>Acetate media</td>
<td>0.25</td>
<td>30.2</td>
<td>NA</td>
</tr>
<tr>
<td>Corn stem carbon</td>
<td>NA</td>
<td>Mini glassy bioreactors</td>
<td>Sewage treatment plant</td>
<td>Acetate media</td>
<td>0.25</td>
<td>31.2</td>
<td>NA</td>
</tr>
<tr>
<td>Rotating carbon brush</td>
<td>Carbon cloth</td>
<td>Tubular MFC</td>
<td>Wastewater effluent</td>
<td>Acetate media</td>
<td>60ᵇ</td>
<td>945ᶜ</td>
<td>210ᵈ</td>
</tr>
<tr>
<td>Carbon nanofiber</td>
<td>Gold foil</td>
<td>Micro-litre size MFC</td>
<td>Primary clarifier influent</td>
<td>Acetate mineral media</td>
<td>0.28</td>
<td>0.083</td>
<td>22,000</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>Gold foil</td>
<td>Micro-litre size MFC</td>
<td>Primary clarifier influent</td>
<td>Acetate mineral media</td>
<td>0.28</td>
<td>0.0234</td>
<td>49,000</td>
</tr>
<tr>
<td>Carbon paper</td>
<td>Gold foil</td>
<td>Micro-litre size MFC</td>
<td>Primary clarifier influent</td>
<td>Acetate mineral media</td>
<td>0.28</td>
<td>0.096</td>
<td>10,000</td>
</tr>
<tr>
<td>Activated carbon granules</td>
<td>graphite plates</td>
<td>fluidized capacitive system</td>
<td>Influent from enriched MFC</td>
<td>Acetate phosphate buffer</td>
<td>11</td>
<td>1.3</td>
<td>NA</td>
</tr>
<tr>
<td>Carbon mesh anodes</td>
<td>Activated carbon</td>
<td>Single chamber</td>
<td>Domestic wastewater</td>
<td>Acetate phosphate buffer</td>
<td>7</td>
<td>NA</td>
<td>1330</td>
</tr>
<tr>
<td>Multi-brush anode</td>
<td>Air cathode</td>
<td>Single chamber</td>
<td>Effluent from MFC</td>
<td>Acetate media</td>
<td>8</td>
<td>4.2</td>
<td>1200</td>
</tr>
<tr>
<td>Porous carbon with a defined pore size</td>
<td>Air cathode</td>
<td>Single chamber</td>
<td>Escherichia coli</td>
<td>Glucose phosphate-buffered basal medium</td>
<td>9</td>
<td>13.4</td>
<td>1606</td>
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<tr>
<td>Granular activated carbon particles</td>
<td>Air cathode</td>
<td>Dual chamber</td>
<td>Effluent from MFC</td>
<td>Acetate media</td>
<td>10</td>
<td>2.6</td>
<td>951</td>
</tr>
<tr>
<td>Tubular bamboo charcoal</td>
<td>Carbon cloth</td>
<td>Tubular two chamber MFC</td>
<td>Effluent from enriched MFC</td>
<td>Synthetic media</td>
<td>NA</td>
<td>NA</td>
<td>1652</td>
</tr>
</tbody>
</table>

A Six corrugated layered anode.
B Cathode surface.
C A/m².
D W/m³.
power generation. However, the power generated is similar to that achieved with a single brush carbon anode (Fig. 6d) MFC system because of cathodic limitations (Liao et al., 2015).

Liu et al. gave a comparative account for carbon-based anode materials, such as graphite, polycrystalline carbon rod (Fig. 6b), carbon fibre veil (Fig. 6c), graphite foil, glossy carbon rod and carbon paper. The maximum achievable current density was estimated by using a well-established biofilm enriched with a domestic wastewater. Both graphite and polycrystalline carbon rods achieved catalytic currents of about 500 μA cm⁻² at 30 °C. In contrast, carbon fibre veil or carbon paper-based material gave ~40% higher current than achieved with graphite rod due to their large accessible surface for microbes (Liu et al., 2010). The rotation of carbon brush anodes used in tubular MFC achieved 2.7 times improvement in performance than achieved with a steady state reactor (Liao et al., 2015). The rotation was effective for achieving adequate nutrient mixing and for minimizing mass transport limitation (Liao et al., 2015).

In general, several studies have indicated that the kinetics of biocatalyst were influenced by the nature and electrode material (Fraiwan et al., 2014). It has also been demonstrated that the internal resistance is one of the important factors which affect the overall performance (ElMekawy et al., 2013).
There has been an increasing preference in using three-dimensional anode structures, such as carbon nanotubes (CNTs), carbon nanofibers (CNF), gold/poly (e-caprolactone) microfiber (GPM), and gold/poly(e-caprolactone), for reducing the internal resistance of MFCs. 3D anode material exhibit lower internal resistance than macroscopic and two dimensional anodes (Fraiwan et al., 2014). Such anode materials are beneficial in increasing the nutrient/proton/oxygen transfer efficiency through the biofilm than with macroscopic carbon paper and planer gold anodes. It has been demonstrated that chemical surface modification of CNT- and CNF-based anodes lowers kinetic losses and cellular toxicity (Fraiwan et al., 2014). Ren et al. (2015) investigated three different CNT-based electrode materials, namely: vertically aligned CNT (VACNT), randomly aligned CNT (RACNT), and spin-spray layer-by-layer (SSLbL)-CNT. The chosen nanotube-materials have very high surface areas to volume ratio of 4000 m$^{-1}$. The results revealed that CNT-based materials attracted more exoelectrogens, Geobacter sp., than the bare gold and, consequently, resulted in a thicker biofilm formation. A maximum power generation density of 3320 W m$^{-3}$ was achieved by using CNTs in a miniature MFC system. This was 8.5 times more than achieved with the 2d-electrode systems (Ren et al., 2015).

2.2. Composite anodes

Composite anodes have attracted considerable interest in recent years. These materials have been used to achieve synergistic effects with two or more materials or by modification of an original material, leading to improved anodic kinetics performance. Table 2 summarises the high performances achieved for MFC construction with composite anodes. As can be observed from these data, a current density as high as 35.7 A/m$^2$ and a power density as high as 3903 mW/m$^2$ can be achieved with some of the reported composite anodes. The different classes of composite anodes are discussed in the following sub-sections.

2.2.1. Graphite-polymer composites

Tang et al. prepared a 3D anode modified with a nanostructured capacitive layer, which composed of titanium dioxide (TiO$_2$) and egg white protein (EWP)-derived carbon assembled core shell nanoparticles. This was integrated into a loofah sponge carbon (LSC) to obtain a high-capacitive 3D electrode, as illustrated in Fig. 7. The coating of the LSC with TiO$_2$ and heat treatment resulted in the decoration of its surface with small particles (Fig. 7b). The resulting anode produced 201% more power than a graphite anode. The enhanced power output was attributed to the boosted electrochemical capacitance of 3D anodes and the synergistic effects between TiO$_2$ and EMP derived carbon, which has good properties, such as high surface area, good biocompatibility, and favourable surface functionalization for extracellular electron transfer (Tang et al., 2015).

Open-celled carbon scaffold (CS) and carbon scaffold – graphite (CS–GR) anodes have been prepared by carbonizing microcellular polyacrylonitrile (PAN) and PAN/graphite composites (PAN–GR) (Wang et al., 2015). The PAN-GR were obtained by foaming with supercritical carbon dioxide (Sc-CO$_2$) as a physical foaming agent. It was demonstrated that the maximum current density obtained with a CS anode was 101% more than obtained with a carbon felt (Wang et al., 2015). The improved performance was attributed to the enhanced hydrophilicity and biocompatibility resulting from carbonization. The use of 3D carbon scaffold anode with hydrophilic functional –C–N group for bacterial colonization was found to improve the extracellular electron transfer (Wang et al., 2015). As demonstrated, three dimensional anodes provide large accessible surface to bacterial biofilm formation (Chen et al., 2015) and, consequently, for achieving high performance MFCs.
Carbon nanofibers modified graphite fibres and reduced graphene oxide/carbon nanotube-coated scaffold are promising new composite anode materials. A maximum current density as high as 35.7 A/m² was obtained from reduced graphene oxide/carbon nanotube-coated scaffold anode system.

Composite anode of graphite fibre brush (MFC-GFB) has been used together with graphite granules (MFC-GG) in a tubular MFC to increase the power density achieved by 5.3 and 1.2 times higher than individually with MFC-GG and MFC-GFB, respectively. The enhanced performance of the system was attributed to the dense biofilm formation and low internal resistance of the system (Li et al., 2013). Fraiwan et al. (2014) recently compared six types of micro-/nano-structured anodes for use in micro-sized MFCs. The anodes considered include carbon nanotubes (CNTs), carbon nanofibers (CNFs), gold/poly (e-caprolactone) microfiber (GPM), gold/poly (e-caprolactone) nanofiber (GPN), planar gold (PG), and conventional carbon paper (CP). The performance of all anodes were tested with compact and reliable micro-litre sized MFC. Table 2 provide a comparison of the performance of all anodes were tested with compact and reliable micro-litre sized MFC. Table 2 provide a comparison of the performance of all anodes were tested with compact
greatly influenced by the ratio of carbon powder and 30% polytetrafluoroethylene (PTFE) solution mixture. The efficiency was tested with an acetate feed MFC, and the power generation was significantly improved with the coating of the anode. Internal resistance of the system was reduced by 59.4%, while power density increased by 1.5 times compared to the use of a non-coated iron net (Yu and Tang, 2015). Fig. 8 shows the SEM images of some composite anodes with polymers. For example, Fig. 8a,b shows the 3D open-celled structure of the carbon scaffold anode which has a diameter of about 5 µm capable of permitting transport of substrate and growth of bacteria colonies that can facilitate extracellular electron transfer from the microorganisms to the anode. Fig. 8c,d also show that the hierarchical micro-/nanostructure displayed by CNFs/GF will also promote the attachment of bacteria to the anode and, consequently, enhance electron transfer simultaneously from the microorganisms to the anode. On the other hand, Fig. 8e–h shows the changes in the structure of an electropun mat as it undergoes stabilization, carbonization and activation.

2.2.2. Carbon nanotubes composite

Recently, the use of CNTs has attracted a lot of interest because of their unique and excellent intrinsic properties which includes high conductivity, corrosion resistance, high surface area and electrochemical stability (Thepsuparungsikul et al., 2012). As an example, carbon nanotube-textile (CNT-textile) have been used for development of high performance MFCs (Thepsuparungsikul et al., 2012; Wang et al., 2015; Xie et al., 2011). The CNT-textile is biocompatible and has high conductivity in nature. The 3D space structure provided by the CNT-textile enables formation of 10 times more biofilm than with an unmodified textile. The space facilitates an efficient substrate transport of biofilm and internal colonization of diverse group of microbial community (Wang et al., 2015; Xie et al., 2011). CNT-textile anode has also been found to produce 10 times less charge transfer resistance ($R_{ct}$). The achievable maximum current density was 157% higher, while the power density was 68% higher and the energy recovery was 141% greater compared with the use of carbon cloth anode (Xie et al., 2011). The CNT-textiles anode is undoubtedly suitable for improving MFC performance. An advanced version of this material is based on coating carbon nanotubes on macroporous sponge (Xie et al., 2012a). The CNT-sponge has lower internal resistance, improved stability, more ordered continuous 3D CNT surface and tuneable structure with improved mechanical stability. Up to 48% higher current density has been achieved with the use of CNT-sponge in MFC compared with that obtained with CNT textile under the same conditions (Xie et al., 2012a, 2011). The use of nanomaterials in the anode not only improved the power generation, but also exhibits tolerance to high substrate concentration. It also enhanced the performance of nanostructured CNFs/GF which enhances extracellular electron transfer from inside of the bacteria to anode hastened by the metabolism of bacteria (Shen et al., 2014).

He et al. also developed a novel upflow fixed-bed microbial fuel cell (FB-MFC) using carbon nanotubes (CNTs) as the anode and microbial carriers for continuous treatment of wastewater and electricity generation. The main focus in designing the FB-MFC was the achievement of an efficient wastewater treatment, while also producing electricity. The maximum removal of chemical oxygen demand (COD) achieved by the reactor was 90%, but it was also observed that the excessive over-loading caused significant electricity generation and COD removal (He et al., 2015).

The use of carbon nanofibers modified graphite fibres (CNFs/GF) composite electrode have also been found to improve performance by up to 7 times better than with the use of unmodified graphite fibres (Shen et al., 2014). The activated carbon nanofiber nonwoven (ACNFN) is an ultra-thin, porous interconnected structure with high bio-accessible surface area. A 3D structure of ACNFN offers maximized surface area for biofilm coverage and when combined with high macroporosity, it enhanced performance through reduction of mass transfer limitation (Manickam et al., 2013). Fig. 9 shows SEM images of some composite anode material and a picture of a ready to use CNT sponge electrode (Fig. 9e). Interestingly, Fig. 9d shows that the CNT sponge has a uniform macroporous structure and provide a 3-D scaffold capable of colonization by bacteria.

2.2.3. Multi-walled carbon nanotubes composite

Multi-walled carbon nanotubes (MWCNTs) with carboxyl groups have been used for air breathing MFC and have been shown to exhibit 2-fold enhancement of power density compared to the use of carbon cloth electrode (Thepsuparungsikul et al., 2012). In a recent study, multi-walled carbon nanotubes/SnO$_2$ (MWCNTs-SnO$_2$/GCE) nano-composite coated on glassy carbon electrode was employed (Mehdinia et al., 2014a). The MWCNTs-SnO$_2$/GCE and bare GCE produced maximum power densities of 1421 mW m$^{-2}$ and 457 mW/m$^2$, respectively (Mehdinia et al., 2014a). In another study, benthic microbial fuel cells (BMFCs) have been significantly scaled up by application of graphite coated with manganese oxide/multiwall carbon nanotubes composites (Fu et al., 2014). The composite offered better hydrophobicity, kinetic activity and power density when compared to plane graphite anode. The observed improvement was due to the combined effect of electron transfer shuttle of Mn ions and their redox reactions on the reaction site (i.e. anode and biofilm) (Fu et al., 2014). Fig. 10 shows the SEM images of MWCNT electrodes. Evidently, the morphologies of the MWCNTs changes considerably when coated on different surfaces and this will influence the achieved performances of the MFC anodes.
2.2.4. Graphene based anode

Graphene is a 2D crystalline allotrope of carbon which has fascinating properties, such as large specific surface area (up to 2600 m$^2$ g$^{-1}$), remarkably high electronic conductivity (7200 S m$^{-1}$), and incredible mechanical strength, i.e. tensile modulus up to 35 GPa (Li et al., 2008; Xiao et al., 2012). Recent studies have also shown that graphene has good biocompatibility (Cheng et al., 2006; Liu et al., 2012) and, can therefore be considered as a potentially useful anode material for MFCs. It has been reported that the power density of graphene modified stainless steel mesh (GMS) was 18 times larger than obtained with a stainless steel mesh (SSM) anode and was 17 times higher compared with polytetrafluoroethylene (PTFE) modified SSM (PMS) (Zhang et al., 2011). The substantial enhancement observed in this case was due to the improved surface area of the electrode, better bacterial biofilm adhesion and efficient extracellular electron transfer (Zhang et al., 2011). The stainless steel (SS) current collector increases electrical conductivity for electrode connections and the performance of the system is improved by the SS current collector which reduced the internal resistance of the system.

Chen et al. (2014) developed a macroporous flexible 3D graphene sponge using an ice template as the anode. The microporous 3D graphene readily allowed proliferation of bacteria in random manner and leads to a high biofilm coverage, resulting in an enhanced performance (Chen et al., 2014). The cost of producing the graphene sponge (G–S) electrode was $2000 per m$^3$ and was, therefore, the least cost efficient by an order of magnitude than any commercial graphite based anode material (Xie et al., 2012b). In another study, the incorporation of tin oxide (SnO$_2$) nanoparticles on the surface of reduced graphene oxide (R-GO-SnO$_2$) was used to achieve power generation which was almost 5 times higher compared with the use of an unmodified reduced graphene oxide (Mehdinia et al., 2014b). Synergistic effects between SnO$_2$ and graphene, as well as good

![Fig. 8. SEM images of composite anodes (a, b) 3D carbon scaffold anodes from polycrylonitrile, (c, d) carbon nanofibers modified graphite felt, ESEM images of (e) PAN precursor, (f) stabilized PAN, (g) carbon nanofibers (CNF), (h) activated carbon nanofibers nonwoven (ACNFN). Reproduced (a and b) from Wang et al. (2015), (c and d) from Shen et al. (2014), and (e–h) from Manickam et al. (2013).]
biocompatibility were responsible for the much improved bacterial biofilm formation and charge transfer efficiency (Mehdinia et al., 2014b). Reduced graphene oxide/carbon nanotubes (R-GO-CNTs sponges) melamine sponges using dip-coating method have also been demonstrated to provide a large electrically conductive surface for Escherichia coli growth and electron transfer in MFC (Chou et al., 2014). Four R-GO-CNT sponges with different thicknesses and arrangements were investigated, but the thinnest one (with a thickness of 1.5 mm) exhibited a superior performance, providing a maximum current density of 335 A m$^{-2}$ (Chou et al., 2014).

The use of a graphene-polyaniline nanocomposite modified anode has also been proposed and found to achieve 3 times higher power generation than carbon cloth (Hou et al., 2013). Significant increment in bacterial loading on the anode surface was observed and could be attributed to the electrostatic interactions between positively-charged ionic liquid (1-(3-aminopropyl)-3-methylimidazolium bromide) functionalized graphene nanosheets (IL-GNS). This improved interaction between bacteria and the anode resulted in the enhanced charge transfer from bacteria to anode (Zhao et al., 2013b).

A 3D reduced graphene oxide–nickel (R-GO-Ni) foam has also been used as an anode for MFC through precise deposition of R-GO sheets onto the nickel foam substrate (H. Wang et al., 2013). The R-GO thickness, in relation to the electrode surface area, can be tuned by loading cycles. This macro-porous scaffold architecture not only

**Fig. 9.** SEM images of some composite anode material. (a) carbon nanotube-textile (CNT-textile) composite, (b) and (c) a 3d-ordered macroporous carbon derived from a natural resource as anode carbon nanotubes (CNT)–sponge electrode, (d) image of the CNT–sponge and (e) picture of a CNT–sponge electrode. Reproduced (a) from Xie et al. (2012a), (b and c) from Chen et al. (2012a) and (d and e) from Xie et al. (2012a).

**Fig. 10.** SEM and FESEM images of MWCNTs-based nanocomposite electrodes. (a) MWCNTs on Porelon membrane and (b) MWCNTs spray-coated on carbon cloth. Reproduced from Thepsuparungsikul et al. (2012).
provides 3D surface for microbial growth, but also enhanced substrate transfer in the culture medium. The performance was substantially improved than with the use of nickel foam and other graphite based anode materials (H. Wang et al., 2013).

The development of a hierarchical porous graphene/nickel anode (G/Ni) was achieved by using *Shewanella putrefaciens* MFCs, which gave 13-fold higher power density than that of conventional MFC carbon cloth anode (Qiao et al., 2014). Considering the low cost of porous Ni and the low weight percentage of graphene (5%w), this composite electrode offers great promise for production of high performance MFCs for larger scale power generation (Qiao et al., 2014).

Some interesting SEM images of graphene-based anodes are shown in Fig. 11. Notable among these, Fig. 11(c,d) shows a comparison of a bare carbon cloth (CC) with R-GO-SnO₂/CC electrodes that have been incubated with bacteria (Mehdinia et al., 2014b). The presence of R-GO and SnO₂ in the latter was obvious. Fig. 10e shows that Ni foam had a smooth surface before R-GO sheets was loaded (Fig. 11f). More clearly, Fig. 10g shows that a continuous 3D scaffold of Ni foam with variable pore size was formed. This microstructure, particularly those with the large pore size, will promote colonization of the inner structure with bacteria and, consequently, enable efficient nutrient transfer (H. Wang et al., 2013). Fig. 11h shows that refluxing the Ni foam in GO solution led to coverage of the whole foam scaffold with R-GO sheets. As a result, a conducting R-GO coating was formed and this could serve as a good electron transfer layer, while also enabling colonization by bacteria and achieving improved power generation (H. Wang et al., 2013). Furthermore, Fig. 11i shows that the R-GO-Ni foam maintains
2.3. Surface modification

The electrode surface plays a significant role in the overall anode quality and performance. Recently, many studies have reported that surface modification is beneficial for achieving high surface areas for bacterial adhesion and enhanced biocompatibility which favours the kinetics of electron transfer. A summary of some of the reported bacterial adhesion and enhanced biocompatibility which favours the surface modification are discussed in the following sub-sections.

2.3.1. Conductive polymer coatings

Conductive polymer coatings have attracted considerable attention due to their high conductivity and biocompatibility (Mehdinia et al., 2013). A composite polyaniline (PANI)-mesoporous tungsten trioxide (m-WO$_3$) has been developed and used as a precious metal free catalyst (Y. Wang et al., 2013). PANI was loaded on m-WO$_3$ via chemical oxidation of PANI. The catalytic activity of the composite was elucidated by using electrochemical techniques. Significant improvement in performance...
was observed with the composite based on the combination of m-WO₃ and PANI. The m-WO₃ exhibited a good biocompatibility, while PANI has a good electrical conductivity (Y. Wang et al., 2013). The changes in morphology caused by this combination is illustrated in Fig. 12. The m-WO₃ displayed a sachima-shaped morphology (Fig. 12a) which became less distinct when loaded with PANI (Fig. 12b). Nevertheless, the ordered pores and pore size were still evident.

Polyaniline (PANI) coated electrodes have been shown to enhance power generation significantly. By using a nanostructured PANI-modified glassy carbon anode, power generation was significantly increased (Mehdinia et al., 2013). Measurement by electrochemical impedance spectroscopy revealed that the charge transfer was significantly enhanced by the nanostructured polyaniline coating (Mehdinia et al., 2013).

The Electrodeposition of PANI networks onto graphene nanoribbons (GNRs)-coated carbon paper (CP/GNRs/PANI) was found to enhance power generation than with the use of GNR and CP (Zhao et al., 2013a). The enhancement was attributed to the positively charged PANI backbone which improved interaction affinity with negatively charged bacterial cells and, thus, enhanced the direct electron transfer via outer membrane cytochromes. Conductive GNRs greatly improved the conductivity of the CP/GNRs/PANI electrode in neutral medium (Zhao et al., 2013a). This observation clearly indicates that the synergistic effect of both component was responsible for the substantial improvement in energy generation (Zhao et al., 2013a).

Carbon nanotubes/polyaniline carbon paper (CNT/PANI carbon paper) was utilised and compared with other traditional carbon paper/cloth in another study (C.-T. Wang et al., 2013). The results demonstrated that a lower ohmic loss and enhanced power generation was obtained with CNT/PANI carbon paper (C.-T. Wang et al., 2013).

Modification of graphite felt (GF) with PANI was followed by the electrotheretic deposition of CNTs. The surface modification resulted in a rough and nano-cilla containing film on the GF. It transformed the surface from hydrophobic to hydrophilic. The use of CNTs increased the surface area for biofilm coverage, as well as for achieving a higher electrical conductivity. The achieved maximum power density of 257 mW/m² corresponds to an increase of 343% and 186%, respectively, when compared with those achieved with the pristine GF MFC and the PANI/GF MFC, respectively (Cui et al., 2015). Also, polyaniline modified stainless steel fibre felt (SSFFs) has been found to offer a low activation overpotential which readily resulted in charge transfer at the biofilm and anode interface (Hou et al., 2015). Fig. 13 shows SEM images of surface modification of anodes. For example, Fig. 13a, b shows that the modified stainless steel fibre felts (SSFFs) have a rough micro-structured surface which is readily conducive to bacteria colonization and improved interaction between resulting biofilm and the electrode.

2.3.2. Graphite/carbon surface treatment

Vertically oriented TiO₂ nanosheets modified carbon paper forms vertically penetrating pores that offer a large contact area to bacteria for direct electron transfer (Yin et al., 2015). This is particularly helpful for improving nutrient distribution, achieving high biocompatibility and favouring electron transport pathways in a recent study (Yin et al., 2015). The maximum power output density of a mixed consortia inoculated microbial fuel cell was increased by 63% by employing a TiO₂–NSs/CP as a bioanode, compared with the use of a bare CP as a bioanode. In another study dual nanofiber mats of TiO₂(rutile)–C(semi-grafito)/C(semi-grafito) was used for MFC anode (García-Gomez et al., 2015), one fibre composed mostly of Ti, O, and C, while the composition of the other fibre was mainly based on C. The dual nanofiber demonstrated a better performance than a single nanofiber. The maximum current density achieved in this study was 8 A/m² (García-Gomez et al., 2015).

In a recent study, two zeolites, namely mobil catalytic materials number 41 (MCM–41) and Sodium X zeolite (NaX), were used to modify graphite felt anodes (Wu et al., 2015). The achieved maximum power density and coulombic efficiency were 152% and 36% higher than those obtained with the unmodified anodes, respectively. Improved performance was due to its microporous structure, super hydrophilicity and enhanced biofilm coverage (Wu et al., 2015). Activated carbon (AC) with SSM (AcM) and Fe₃O₄ anode has also been explored for MFCs and the performance of the system was attributed to the enhancement of capacitance (Peng et al., 2012). Nano-goëthite with 0%, 2.5%, 5.0% and 7.5% (mass percentage) were added into the activated carbon (AC) powder and rolled onto stainless steel mesh. The resulting composite anodes produced 36% higher power than with an unmodified AC anode. The increased performance was achieved because of decreased charge transfer resistance (Rct) and increased exchange current density (Iₒ) (Peng et al., 2013).

A number of studies have demonstrated that MFC start-up time can be lowered by electrochemically oxidizing carbon mesh in nitric acid or ammonium nitrate. It was demonstrated in one study (Cai et al., 2013) that the anodes modified by this approach achieved a Coulombic efficiency of 71%. Oxygen-containing functional groups present on the carbon surface may be responsible for the improved overall performance of the system (Luo et al., 2013). Carbon cloth (CC) anodes treated with concentrated nitric acid and heated in a muffle furnace (CC-H), gave 0.42–0.46 V for CC, 0.52–0.58 V for CC-A and 0.80 V for CC-H across a 1000 Ω resistance. SEM images confirmed that the high biofilm density on CC-H was responsible for the higher voltage and current generation (Cai et al., 2013).

Also carbon veil (CV) and carbon cloth (CC) modified with a microporous layer (MPL) have been used for MFCs and the power generation from the modified anodes almost doubled those achieved with the unmodified electrodes (You et al., 2014). The 3D macroporous anodes
based on stainless steel fibre felt coating carbon nanoparticles (graphene, carbon nanotube, or activated carbon) on stainless steel fibre felts (SSFFs) provided large accessible surface area for biofilm growth due to their morphologies and structures, as well as interfacial substrate transport. It also offers advantages in terms of kinetics, such as low overpotential and high reactivity (Hou et al., 2014). Fig. 14 shows the SEM images of surface treated anodes. The presence of interconnected and entangled dual nano-fibre which formed a non-woven mat is obvious in Fig. 14a. On the other hand, Fig. 14b shows that the carbon fibres were more densely woven on the carbon cloth than on carbon veil (Fig. 14f, h). In contrast, those formed on microporous layered (MPL) surface were uneven and more porous which may result in better and higher surface area for bacterial growth. Overall, stainless steel fibre felt, carbon nanotube/polyaniline carbon paper, and nanostructured polyaniline-coated anode were some of the high performing anodes based on surface modification that achieved power densities of 2142 mW/m², 1574 mW/m² and 820 mW/m², respectively (Hou et al., 2013).

2.4. Metal-based anode

In the last ten years, many metals such as titanium (ter Heijne et al., 2008), gold (Crittenden et al., 2006; Richter et al., 2008), and copper (Zhu and Logan, 2014) have been considered for use as anodes in MFCs. Most of these metals were unsuitable because of their corrosive nature. In contrast, stainless steel has attracted increasing interest for use as an anode material for microbial fuel cells (Pocaznoi et al., 2012). The performance of some of the reported metal based anodes are summarised in Table 4. Evidently, the performance of stainless steel as an anode material stands out from the rest. Pocaznoi et al. have compared stainless steel anode with carbon cloth and graphite plate for use as anodes for MFC with the use of soil landfill and acetate as substrate. Fig. 15 shows the ability of carbon and stainless steel materials to form microbial anodes under identical conditions. In all cases, the biofilm formation was reasonably uniform with almost complete coverage. This study found that carbon cloth anode produced a current density of 33.7 A/m², while SS anode produced 20.6 A/m² (Pocaznoi et al., 2012). The achieved high power with the 3D structure carbon cloth was due to its high surface area. Electrochemical testing of stainless steel at +0.1 V vs. SCE provided up to 35 A/m² (Pocaznoi et al., 2012). It has also been demonstrated that oxidised stainless steel is a more effective anode material, and a facile SS modification gave a current density up to 45.3 mA/cm³ at ambient temperature. This is the highest current generation reported to date (Ledezma et al., 2015). From all studies it is clear that stainless steel is a more efficient and cost effective anode material for future development of MFCs. But some key factors must still be considered, such as corrosion resistance, and achievable surface area to achieve high performance MFCs. There is still a lot of room and scope for improvement in metal anode development. Planar gold was found to be best performing metal anode with a power density of 8000 mW/m².

3. Challenges and future directions

One of the long-term goals of MFC technology is to advance capabilities that will enable the utilization of the vast volumes of wastewater that are readily available globally, as a basis for generating an alternate large scale energy. If achieved, this will have the dual benefits of “deriving energy from the problem itself”, while also alleviating the various environmental impacts often associated with wastewater. However, before the operation of a commercial plant can be realised, many challenges are yet to be overcome. To date, the implementation of large scale MFC technology has been hindered by low power generation and high material costs. Further research are therefore still needed to develop low cost, sustainable, high performance materials that can be used for development of efficient MFC systems.
Recent studies have demonstrated that the use of 3D materials for MFC anodes have huge potential for supporting the development of high performance MFCs in the future because of their demonstrated ability to increase power generation by several orders of magnitude. In this regard, further future consideration must also be given to the development of MFC stacks as a way of increasing the net power.

![Micrographs of TiO$_2$–C/C dual nano fiber calcined at 1000 °C for 3 h at N$_2$ atmosphere, (b) MCM-41, (c) NaX, FESEM images of the bare CP electrode, (d) TiO$_2$-NSs/CP electrode, (e) TiO$_2$-NSs/CP electrode obtained under optimal conditions, SEM images of anode electrodes, (f) CV20 (20 layered carbon veil), (g) CV30 (30 layered carbon veil), (h) CC, (i) CV20-MPL, (j) CC-MPL, and (k) MPL structure on CC-MPL. Reproduced (a) from Garcia-Gomez et al. (2015), (b, c) reproduced from Wu et al. (2015), (d, e) from Yin et al. (2015), and (f–k) from You et al. (2014).]
Table 4
Comparisons of the performance of some metal based anodes used for MFCs.

<table>
<thead>
<tr>
<th>Metal based</th>
<th>Anode</th>
<th>Cathode</th>
<th>System architecture</th>
<th>Source of inoculation</th>
<th>Substrate</th>
<th>Anode surface area (cm²)</th>
<th>I max (A/m²)</th>
<th>Pmax (mW/m²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stainless steel</td>
<td>NA</td>
<td>Three-electrode cell</td>
<td>Soil leachate</td>
<td>Acetate substrate</td>
<td>2.5</td>
<td>35</td>
<td>NA</td>
<td>(Pocaznoi et al., 2012)</td>
</tr>
<tr>
<td></td>
<td>Oxidised stainless steel</td>
<td>NA</td>
<td>3-pin electrochemical cells</td>
<td>Effluent from MFC M1 medium</td>
<td>NA</td>
<td>2</td>
<td>0.0453*</td>
<td>NA</td>
<td>(Ledezma et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>Bare gold</td>
<td>Air cathode</td>
<td>Miniaturized microbial fuel cell</td>
<td>Anaerobic digestion sludge</td>
<td>Acetate medium</td>
<td>1.11</td>
<td>480</td>
<td>8000</td>
<td>(Ren et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>Planar gold</td>
<td>Gold foil</td>
<td>Micro-litre size MFC</td>
<td>Primary clarifier influent</td>
<td>Acetate mineral media</td>
<td>0.28</td>
<td>0.117</td>
<td>8000</td>
<td>(Fraiwan et al., 2015)</td>
</tr>
</tbody>
</table>

* A/cm³.

Fig. 15. Macroscopic and fluorescence images of anodes with and without biofilms on (a) carbon cloth, (b) smooth stainless steel, (c) macrostructured smooth stainless steel and (d) microstructured smooth stainless steel. Images from left to right are: macroscopic view of the clean electrode, epifluorescence image and treated image for assessment of biofilm surface coverage ratio. Reproduced from Pocaznoi et al. (2012).
4. Conclusion

The proper and effective choice of an anode and the material from which it is made is a critical factor in the effort to achieve high performance MFCs. The choice of the wrong anode material will render this possibility redundant. As the kinetics of the microbes employed in MFCs are much sluggish than those achievable with a cathode material or cathode catalyst, the use of 3D anodes have been demonstrated to date to be very beneficial and capable of increasing power generation by several orders of magnitude compared with the use of 2D plane anodes. Admittedly, there is still much to be done to further improve efficiency before large scale power generation from wastewater can be realised. In addition, consideration of intrinsic parameters, such as kinetics, internal resistance, surface anatomy and interaction of surface with biofilm, are also necessary. Further development of new cost effective and efficient materials is also needed for construction of new renewable and sustainable MFCs which can be deployed in wastewater treatment plants.

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Chen, W., Huang, Y.-X., Li, D.-B., Yu, H.-Q., Yan, L., 2014. Preparation of a macroporous three-dimensionally ordered macroporous carbon film, are also necessary. Further development of new cost effective and efficient materials is also needed for construction of new renewable and sustainable MFCs which can be deployed in wastewater treatment plants.

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