The Role of Microfabrication and Nanotechnology in the Development of Microbial Fuel Cells

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Abstract: Innovative solutions are paramount to our identification and development of alternative energy resources, specifically for the production of potable water. Microbial fuel cell (MFC) is a trending emerging technology that promises green energy production while simultaneously treating wastewater. At present, several research efforts are working towards determining which bacteria, fuels and materials are optimal for developing the most efficient MFCs; micro-sized MFCs have a key role in this goal. Therefore, in this review, we summarize recent microfabrication techniques for building micro-sized cells and elaborate on their advantages and the challenges that need to be overcome. We will then focus on the integration of nanomaterials into MFCs and finish with an overview on the challenges to scaling-up MFCs and potential uses for these miniature cells.

1. Introduction

As the human population continues to expand exponentially, expected to surpass 8 billion by 2030, so are the demands for water and energy. Inadequate access to clean water has been identified as one of the most critical challenges to human health worldwide.^[1-2] A network exists between energy conversion and the production of potable water. Most advanced water treatment and desalination techniques, such as reverse osmosis, require large amounts of energy to operate, while power plants require large amounts of water to convert energy.^[1] Moreover, water and energy also have a direct impact on food and the environment. Consequently there is an increased need for not only more efficient technologies to treat water and convert energy, but also to innovate strategies that make technology more affordable, more easily accessible and with the lowest environmental impact possible.

Microbial fuel cells (MFCs) have the potential to join the energy-water network in a way that could resolve some of these challenges. Microbes (exoelectrogenic bacteria), naturally found in wastewater, are capable of transferring electrons beyond their cellular membrane. These bacteria can gain energy during respiration by the transfer of electrons to external acceptors.^[3-6] Under natural conditions, oxygen can act as the electron acceptor; however, by engineering an anaerobic chamber (anode), a conductive electrode can be converted into the main electron acceptor. This enables a chemical catalyst in the cathode chamber to reduce the number of transferred electrons generated in the anode. Bacteria can, therefore, behave as a biological catalyst, participating in the conversion of an electron-rich fuel (organic matter) into useful electricity, while simultaneously reducing the organic waste in the water.^[7-8]

Although many studies have investigated the mechanisms involved,^[9-10] how electrons are transferred from bacteria to the electrode remains unclear. At present, we understand that there are several electron transfer methods including mediated and direct transfer.^[11-15]

Currently, many groups are focused on optimizing this promising technology and bring it to a commercial stage for the simultaneous mass conversion of energy and water treatment.^[16-18] An important strategy involves determining which bacteria, fuels and materials are optimal for developing the most efficient MFCs; micro-sized MFCs provide a platform for more efficiently testing these variables.^[19-20] Micro-sized MFCs have some advantages over their macro counterparts, as has been shown by *H.-Y. Wang et al.*^[19] For example, micro-sized MFCs have a higher mass flux density per unit area, which can lead to a much faster start-up time compared to larger cells. This makes it possible to perform a preliminary, rapid assessment that can identify new active microbes, as well as novel materials and fuels. Moreover, micro-sized MFCs have larger surface-area-to-volume (SAV) ratios, meaning larger surfaces for reactions, mass transport and the transfer of electrons, which translates into more efficient usage of fuel per unit volume. Finally, the proton diffusion length from anode to cathode electrodes can be considerably reduced, which reduces resistance and ultimately losses. Additionally, since micro-sized MFCs are essentially miniature energy scavengers, they can also be useful power sources for lab-on-a-chip applications and integrated onto chips for low-power electronic devices or sensors.^[21]

At present, a type of microfabrication technology called nanotechnology is being used to investigate and implement variations in the development of micro-sized MFCs with the aim of optimizing MFC performance. The benefits of the higher SAV ratio that is intrinsic to objects with smaller dimensions can be further exploited by using arrays of nanostructures, such as forest-like formations, which also amplify the available surface area. In addition, electrical, optical and mechanical properties can be tuned and optimized through the transformation of certain materials into nanosized structures.^[22]

Therefore, micro-sized MFCs are being developed using standard microfabrication techniques with novel nanomaterials. Many groups have capitalized from using tools like micro- and nanofabrication techniques by developing numerous devices and testing several materials, microbes, fuels and architectures, as will be described during this review. We will summarize some efforts to use microfabrication techniques to build miniature devices and elaborate on their advantages and challenges. We discuss the integration of nanomaterials into MFCs and finish with an overview on the potential to scale-up MFCs to the commercially available level and some potential applications.

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Figure 1. Simplified schematic representation of several microfabricated microbial fuel cells with components. a) Silicon substrates for both anode and cathode, b) PDMS-based chamber for both anode and cathode, c) silicon substrate for the anode and a PDMS-based chamber for the cathode and d) air-cathode architecture with the anode on silicon and a polymer as a gasket to complete the chamber.

2. Microfabricated MFCs

Over 50 years of development in the semiconductor industry has led to the development of numerous additive and subtractive techniques that compose an amazing set of tools for building a world of miniaturized devices.^[23] Specifically, developments in photolithography, a technique that relies on light to transfer incredibly small patterns onto photosensitive materials, have catapulted the fabrication of integrated circuits, in line with Moore's law.^[24] Advances in photolithography have benefited not only integrated circuits, but they have also encouraged new technologies to arise. For example, the development of micro electromechanical systems (MEMS) has greatly impacted our daily lives.^[25]

Over the past few years, several attempts using microfabrication have been used to develop smaller and smaller MFCs. Figure 1 shows simplified schematics of the cells' components and architectures that will be described next. As early as 2003, *Chiao et al.* fabricated a miniature MFC using microfabrication techniques to pattern a silicon wafer (wet anisotropic etchant, KOH:H₂O = 1:2 by weight at 80°C) with micro-channels coated with gold (thermal evaporation of 20 nm/250 nm of Cr/Au) to serve as an electrode. The anode and cathode were fabricated identically and separated by a proton exchange membrane (PEM) (Figure 1a). The micro-patterns increased the SAV ratio up to five times that of a planar electrode. This caused an increase by 5 orders of magnitude in power density compared to a similar cell that was previously fabricated by the same group through the use of macro-scale machining processes. However, improvements were necessary to increase its low efficiency (0.027%) due to difficulties with appropriate sealing and electric contacts from anode and cathode.^[26] Later, *Siu and Chiao* used polydimethylsiloxane (PDMS) stamps fabricated with soft photolithography techniques, featuring micro-pillar array structures coated with gold (electron-beam evaporation of 50 nm/200 nm of Cr/Au) to serve as the anode and cathode (Figure 1b). Efficiency was most likely improved (9–14%) due to enhanced sealing and increased SAV ratio. More interestingly,

this study used human plasma as fuel for the bacteria, which showed the potential for in vivo applications. In fact, the main structural material, PDMS, is a biocompatible material with diverse applications in several technologies including microfluidics.^[27]

Soon after, *Qian et al.* proposed a stacked architecture that integrated a gold anode (evaporation of 20 nm/500 nm of Ti/Au) with a photoresist-based anode chamber (100-μm thick SU-8) and a PDMS-based cathode chamber (formed by soft photolithography) (Figure 1c). Using this technique, they obtained a very small anode volume (1.5 μL), and although the performance was satisfactory, the internal resistance was high (about 30 kΩ);^[28] high internal resistance is an inherent

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challenge for micro-sized MFCs because their smaller contact area means that proportionately they have considerably more contact with the electrolyte and therefore higher electrolyte resistances.^[19] In the following subsection, we will review some strategies from the microfabrication perspective that aim to reduce contact resistance.

Thereafter, the same group extended their design by developing a 4- μL MFC, which consisted of a double PDMS chamber separated by a membrane with carbon-cloth (CC) anode and cathode electrodes (similar to Figure 1b but with CC instead of gold electrodes). Both PDMS-based chambers were fabricated with soft photolithography, which then sandwiched the membrane along with the carbon-cloth electrodes. The carbon-based electrodes increased the SAV ratio, improving both efficiency and internal resistance to achieve a remarkable power density of 62.5 W m^{-3} .^[29] Later, *Choi et al.* reported a MEMS-based MFC that produced even higher power densities. They produced 4.5- μL anode and cathode chambers by spin coating a 20- μm -thick photo-definable PDMS-based film on top of a glass substrate (similar to Figure 1b but with glass substrates containing the electrodes and sandwiching the device). The glass substrates were first coated with gold (electron-beam evaporation of 20 nm/200 nm of Ti/Au) and then patterned with photolithography and the lift-off process to define the electrodes ($1.5 \text{ cm} \times 1.5 \text{ cm}$). They achieved a relatively high efficiency of approximately 30% as a result of several factors: a short proton diffusion length, highly efficient anode-respiring bacteria and a large contribution by tight sealing and the inclusion of L-cysteine (O_2 scavenger), which minimized oxygen intrusion. Internal resistance was estimated at $10 \text{ k}\Omega$, which was an improvement, although still a high value. Using this design, *Choi et al.* produced a remarkable power density of 2300 W m^{-3} .^[30]

More recently, creativity in microfabrication techniques has provided different perspectives of MFCs that have contributed to data discovery and new analyses. For example, *Dai et al.* fabricated a transparent, micro-sized MFC for both optical and electrical analyses of biofilm formation. Using this device, they gained insight into bacterial growth and the electron transfer processes in MFCs. The cell was fabricated using laser micromachining, which patterned seven layers of transparent polymethyl methacrylate (PMMA), defined the electrodes by depositing 10 nm of Cr/Au and finished the assembly by manual alignment and thermal bonding (100°C for 1 hour).^[31]

Currently, the record for highest power density among all micro-scale MFCs is the one fabricated by *Ren et al.*, which showed 3300 W m^{-3} with an outstanding Coulombic efficiency of 79%. These results were possible thanks to a very small characteristic length between electrodes, which allowed an improvement in both SAV ratio and mass transfer coefficient while the diffusion-layer resistance is highly reduced.^[32] It should be noted, however, that this design involves the continuous flow of anolyte and catholyte solutions at specific rates, thus requiring the use of external energy, which is far from an ideal condition for any practical scenario, especially for the catholyte solution.

2.1. Contact engineering in micro-sized MFCs

As we highlighted earlier, improving contacts can help to considerably reduce contact resistance in micro-sized MFCs. This is especially important when silicon is not only the support material in a microfabricated MFC, but it also takes part in the electrical circuit of the cell. Since silicon can play a very important role in many of the current techniques for nano-structure-formation, such as nanowires (NW) or carbon nanotubes (CNT) growth, which at the same time are growing in importance in the development of microfabricated MFCs (Section 3), it is imperative to attain a comprehensive understanding of the different contact schemes in semiconductor materials.

Figure 2. Simplified band diagrams and current-voltage characteristics of Schottky and ohmic contacts.

Contact engineering techniques are essential to the semiconductor industry and frequent improvements contribute to establishing the maximum output current (and ultimately the power) from energy harvesters like MFCs. In a contact material study for microfabricated MFCs, Schottky and ohmic contacts must be investigated. Schottky contacts have a metal-semiconductor connection, which can form a potential energy barrier with rectifying characteristics (current is allowed to flow in only one direction), while ohmic contacts are junctions between two conductors that lower resistance without blocking, thereby facilitating easy bidirectional current flow.^[33]

Schottky contacts can behave more like ohmic contacts if they manage to reduce their barrier enough to let the current flow. Figure 2 shows schematic representations of both Schottky and ohmic contacts, which depicts their behavior. Some strategies can be used to achieve a lower barrier such as ion implantation of electrically active dopants into the silicon, which reduces resistivity and thus lowers the barrier. Another effective technique is the formation of conductive compounds with silicon such as forming silicides through metal deposition and a thermal process. Common silicides used in the semiconductor industry nowadays are nickel silicide (NiSi), and cobalt silicide (CoSi_2).^[34-35] With these concepts in mind *Mink et al.* have investigated the

use of standard microfabrication techniques to reduce contact resistance. They used aluminum, another industry standard contact material, and cobalt, which can form a silicide with reduced resistance and improved contact performance. As expected, ohmic contact materials outperformed their Schottky counterparts in current production and in some instances in power as well. In particular, ohmic aluminum contacts produced the highest current, while ohmic cobalt contacts are considered preferable for compatibility with integrated circuits for the smallest integration requirements.^[36] This study showed that improvements in contact engineering are important for device engineering and for microsystems. More in-depth studies on a larger variety of metal contact materials should be performed to better understand which ohmic metal is best for MFCs and their intended application.

2.2. Arrays of micro-sized MFCs

Recently, *Hou et al.* have demonstrated the feasibility of using advanced microfabrication methods to fabricate MFC arrays with the purpose of offering a pragmatic path to make direct and in parallel comparisons between different microbes and other parameters. The system consisted of 24-individual air-cathode micro-sized MFCs integrated onto a single chip. In particular, this array used environmental samples to validate the utility of the MFC array system and two previously identified isolates, *Shewanella* and *Arthrobacter*, which showed enhanced electrochemical activities of 2.69 mWm^{-2} and 1.86 mWm^{-2} , respectively, validating results from large-scale conventional air-cathode MFC experiments. This parallel air-cathode MFC array system is an exciting development that is expected to promote and accelerate the discovery and characterization of many more electrochemically active bacteria.^[37]

With a different aim in mind, *Choi et al.* reported an array of three micro-sized MFCs connected in series with the intention of increasing generated voltage levels. The three MFCs ($50 \text{ }\mu\text{L}$) consisted of a two-chamber design formed by two $500\text{-}\mu\text{m}$ -thick polytetrafluoroethylene gaskets, sandwiched by two glass slides and separated by a cation exchange membrane (CEM). MFCs with a *Geobacter*-enriched mixed bacterial culture as the anolyte and ferricyanide as the catholyte were independently injected into the chambers. The advantages of this MFC array included an outstanding 100 mW of total power and an output voltage of 1.8 V , but was disadvantaged by a high internal resistance and voltage reversal, in which one or more cells reversed its/their polarity, reducing the power generated.^[38] Voltage reversal can occur when one cell does not generate enough current or voltage compared to the other cells because of insufficient nutrients or microbial activity.^[39] In fact, similar problems appeared in a series array of three of these single-feeding, microfabricated, air-cathode, membrane-free microbial fuel cells ($40 \text{ }\mu\text{L}$ each). Non-uniformities in assembly and the single-channel feeding system caused both high internal resistance and the voltage reversal effect, which ultimately limited the power density (45 mWm^{-3}) of the array.^[40]

2.3. Microfluidic MFCs

Finally, some groups have capitalized the use of laminar flow to separate the anode from the cathode without the use of a proton exchange membrane, which can be expensive and add resistance to the system (Figure 3).

Li et al. reported the smallest MFC (total volume of $0.3 \text{ }\mu\text{L}$) by using techniques similar to previous cell fabrications—on a glass substrate with patterned gold electrodes (sputtering of $50 \text{ nm}/100 \text{ nm}$ of Cr/Au , patterned with photolithography and wet etch) and a PDMS stamp on top; these were fabricated with standard soft photolithography to encapsulate the cell.

Figure 3. A representation of a microfluidic MFC with laminar flow.

However, the main difference from previous designs was their horizontal arrangement of the anode and cathode to circumvent the use of a membrane to separate them. Power was dependent on the strain of bacteria used, $18.4 \text{ mA}\text{m}^{-2}$ by *Geobacter sulfurreducens* and $25.4 \text{ mA}\text{m}^{-2}$ by *Shewanella oneidensis*, and on the specific mechanism of electron transfer and oxygen tolerance.^[41] Using the same methodology, *Wang and Su* developed a microfluidic MFC with laminar flow for rapid detection of electrochemical activity of microorganisms. As described above, gold electrodes were used on a glass substrate (electron-beam evaporation of $30 \text{ nm}/100 \text{ nm}$ of Cr/Au , patterned with photolithography and wet etch) and fitted with a PDMS stamp. The MFC differentiated between active and inactive microflora yielding a 115 mV difference in open circuit voltage.^[42]

3. Nanomaterials in micro-sized MFCs

To further improve micro-sized MFC performance, many have opted to integrate nanomaterials as optimized and biocompatible electrodes.^[43] One of the most promising candidates we would like to discuss are carbon nanotubes (CNT) because they have efficient mechanical and electrical characteristics, a large surface area and are biocompatible^[44–45] (as evident from Figure

4a). Additionally, usage of different nanocomposites materials in both research and industry is growing rapidly because they can be valuable electrode alternatives that offer improved electrical properties at a competitive cost.^[43, 46] Initially, studies were performed to show composite materials of cloths with incorporated nanotubes for improved performance. *Tsai et al.* increased the power density (up to 250%) and reduced internal resistance using carbon-cloth electrodes coated with multi-walled carbon nanotubes (MWCNTs).^[47] Similarly, *Sun et al.* modified carbon paper with a layer-by-layer assembly technique to form a coating based on electrostatic interactions between polyelectrolyte polyethyleneimine, a positively charged polymer solution and a negatively charged MWCNT solution. This strategy ensured a high content of MWCNTs with a large accessible surface area, which helped to decrease the resistance in the MFC and enhance the power density by 20%.^[48] Likewise, *Xie et al.* developed a CNT-textile composite as an enhanced anode electrode. The 3-dimensional macroscale porous structure had a superior biofilm interaction with 10 times more surface area and a lower resistance. Once the MFC was equipped with the CNT-textile anode, the maximum power density increased by 68% compared to a conventional carbon-cloth anode.^[49] Although most of the studies focused on improving the anode electrode, there have been also studies that aim at the cathode. For example *Liu et al.* developed a MnO_x -based nanostructured material as an effective cathodic catalyst for enhanced oxygen reduction in MFCs.^[50] This kind of novel materials represents a relevant improvement, which could be a valuable alternative to the more expensive Pt-based catalyst.

Next, researchers aimed to resolve the challenge of electrically connecting microfabricated MFCs effectively with CNTs. *Mink et al.* fabricated relatively small microsized MFCs (1.25 μL anode volume) that featured an anode consisting of a forest of MWCNTs, which incorporated a nickel silicide (NiSi) ohmic contact area with the aim of reducing contact resistance. These microsized MFCs were vertically stacked in a two-chamber architectural design (similar to the design in Figure 1c) with an anode fabricated on a highly doped silicon wafer with high conductivity. The nickel silicide contact pads were formed by deposition and lift-off of nickel (20 nm of Ni by e-beam evaporation process) and completed by annealing for 30 seconds at 450°C. Next, reactive-ion etching was used to form the 50- μm -deep anode chamber. The CNT process began with the deposition and patterning (lift-off process) of the metal catalyst layer (200 nm/65 nm of Cr/Ni by sputtering) and the growth process in a plasma-enhanced chemical vapor deposition system to a height of approximately 40 μm with acetylene (C_2H_2) and ammonia (NH_3) as carbon source gases at 650°C–700°C. Finally, the CNTs were functionalized (in sulfuric acid for 2 hours) to remove residues of the metal catalyst and other impurities, as well as to improve cell adhesion by generating carboxylic groups around the CNTs. The result was a cell with remarkable current and power densities of 197 mA m^{-2} and 392 W m^{-3} , respectively. The enlarged anode SAV ratio and low ohmic contact area resistance are expected to have improved transfer and transport of electrons.^[51]

Later on, *Inoue et al.* developed a miniaturized MFC using micro and nano features in an optimized electrode structure. Two fundamental approaches to optimize power generation are addressed in this work: first, the use of micrometric configurations to increase surface area and second, enhanced electron transfer between bacteria and nano interfacial structures (e.g., CNTs) through nanowire pili in the microbes. The first strategy with microchannels caused power production to increase up to ~140% compared to a flat electrode; however, by incorporating CNTs on top of the microchannels the power increased by up to ~200%.^[52]

Figure 4. a) SEM image of a biocompatible CNT-based anode with bacteria. Reprinted with permission from ref. [51]. Copyright 2012 American Chemical Society. b) Power generation by *Mink et al.* reactor for different anode-electrode materials showing a maximum output for the CNT-based anode. Reprinted with permission from ref. [53]. Copyright 2013 American Chemical Society.

Mink et al. reported two sustainable and forward-looking MFCs. The first was a single-chambered air-cathode microsized MFC (75 μL) that uses complementary-metal-oxide-semiconductor - compatible processes and has MWCNTs as an on-chip anode (architecture as in Figure 1d). The performance of this device was compared with gold, commonly used as an anode material despite its great expense, and with nickel, a more inexpensive substitute. This design features an air-cathode that uses oxygen as its electron acceptor. Moreover, in this model the need for an expensive membrane and the replenishment of the catholyte (ferricyanide solution) was removed. As expected the MWCNT

anode outperformed the others in both current and power densities by ~ 6 and ~ 20 times, respectively (Figure 4b illustrates this enhanced power production). The devices ran for over 15 days, indicating stable and high-endurance power generation, sufficient to feed ultra-low-power electronics over long periods of time.^[53] The second cell reported had a pragmatic, mobile and inexpensive design that can be fueled with human saliva. This micro-sized MFC (25 μL) also consisted of a single-chambered air-cathode, but features a 2-dimensional atomic crystal-structured graphene material as an anode. With the high organic content of saliva as a fuel, the device produced higher current densities (1190 A m^{-3}) than any previous air-cathode micro-sized MFC. Moreover, the graphene anode generated 40 times more power than that possible using a carbon-cloth anode. These findings invite exploration into alternative, innovative and sustainable fuels, especially useful for lab-on-a-chip devices or portable point-of-care diagnostic devices.^[54]

More recently, *Ren et al.* performed a study with three different CNT-based electrode materials: Vertically Aligned CNT (VACNT), Randomly Aligned CNT (RACNT), and Spin-Spray Layer-by-Layer (SSLbL) CNT. Two important conclusions can be drawn from the experiment: (i) thicker biofilms are formed on the CNT-based electrodes compared with bare gold, which suggests a higher attraction from the bacteria towards the nano-structures. (ii) Among the three CNT-based materials, the thickest biofilm was formed on the electrode with the lowest sheet resistance (SSLbL-CNT), which, at the same time, led to higher power generation (3320 W m^{-3} , record power density shared with reference [32]).^[55] Nevertheless, with a similar design as in reference [32], both anolyte and catholyte solutions are continuously pumped into the chambers, which is not a practical scenario as mentioned earlier.

4. Scaling up and commercialization

MFCs have the potential to become a sustainable source of electricity while simultaneously treating water; however, their benefits will only be realized if they can be commercialized. First, more efforts to increase power density are necessary to identify a suitable niche market. Secondly, compensation for increased resistances and overpotentials as well as other size-dependent effects demand more attention to scalability. And thirdly, the appropriate choice of materials for a balanced trade-off between performance, endurance and cost is necessary.^[56–57]

Ideally, sufficiently high-power density levels could make water treatment an energy-profitable process such that no external power source is needed and environmental impact is minimal.^[58] Most efforts have focused on optimizing electrodes and architectures, while fewer have concentrated on studies and models of both microbial and electrochemical activities, whose deep understanding could lead ultimately to power generation and performance enhancement.^[57] Results from all of these studies and mathematical models highlight a few key elements to increase MFC performance. First of all, we have to realize that MFC size does considerably affect cell performance: as MFC size decreases, volumetric power density increases.^[59]

Moreover, electrode over-potentials in small cells can be decreased by increasing the surface area of the anode.^[60] Therefore it is important to carefully interpret results from miniature cells and learn how to extrapolate conclusions into implementation of bigger cells as scaling-up effects will impact the final performance. Such effects can be as diverse as MFC geometry and architecture, to the solution conditions like conductivity and substrate concentration. *Dewan et al.* first determined that the maximum power density is proportional to the logarithm of the anode's surface area rather than directly proportional to the anode's surface area.^[59] However, *Dekker et al.* expanded this concept to show that this relationship does not necessarily always hold; new challenges arise from scaling-up that are not evident from smaller laboratory setups where power production is limited.^[61] From further investigation into effects from scaling up, *Chen and Logan* concluded that cathode surface area could play a more important role in power optimization of larger cells. For example, they found that doubling cathode size increases power by 62%, while doubling anode size increases power by only 12%. Therefore, volumetric power density appears to be a direct function of cathode-specific surface area, suggesting that upon scaling up, the cathode becomes the more important electrode for obtaining higher power densities from MFCs.^[62]

Another important consideration for increasing power production and decreasing internal resistance is the separation between electrodes. *Liu et al.* showed that to preserve the power density at scaled-up sizes, electrode spacing must remain the same or even be reduced.^[63] Using a somewhat different concept, *Zhang et al.* later studied how the combined use of brush anodes, separators and supporters can produce a scalable MFC architecture. The separator is essential by preventing undesirable contact between electrodes and oxygen leakage into the anode. To resolve these concerns, MFCs were designed with closely spaced electrodes and an added second cathode, which doubled the power generation (from 75 W m^{-3} with a single cathode to 154 W m^{-3} with two cathodes).^[64] These results are in line with those of *Chen and Logan*.

In terms of mathematical models, only a few attempts have been currently developed taking into account several of the complex variables involved in MFC design (including electrochemical models, biofilm models and bulk-liquid models). For example, *Zeng et al.* came up with a model that integrates biochemical as well as mass/charge interactions, simulating both steady and dynamic behavior to study the effect that several parameters have on the power generation. Such model can be a powerful and efficient tool to investigate scaling-up effects and help during the design process of more efficient MFCs.^[65] However, in many cases the models include exhaustive calculations that mainly define anode transport and its biochemical phenomena, but most of the times ignore relevant information from the cathode side.^[66–68] A more useful approach at the moment would be to implement simpler models that can help to estimate MFC performance given the following three main factors: (i) the impact of each single losses, (ii) charge and mass transport phenomena on both anode and cathode chambers and (iii) biofilm formation.^[57, 65]

On the other hand, power management may be equally as important as power generation. Because energy sources can be intermittent, an adequate power management system is necessary to condition and produce a useful power signal for actual application. Although capacitors and DC/DC converters have been demonstrated to maintain standard voltage outputs (1.5 V or 3.3 V) compatible with electronic devices,^[69] there is room to optimize designs to increase efficiency and maintain the available maximum power output. A couple of very recent and good examples of efforts toward this direction are the work by *Carreon-Bautista et al.* and *Zhang et al.* The former have demonstrated a fully integrated DC-DC converter working as an energy-aware power management unit (EAPMU) for MFC arrays, which includes an efficient maximum power point tracking (MPPT) system that allows dynamically adaptation to different input cells. It achieved a maximum efficiency of 65% for 1.6 mW of input power and 1 mA load current.^[70] The later interfaced a 50 μ L CNT-based MFC with a pulse-frequency modulation type DC-DC boost converter, which provides a load independent output voltage of 0.9–1.2 V with a peak efficiency of 85% at a 9 μ W load.^[71]

From an economic standpoint, it is of utmost importance for scaling-up applications to reduce capital costs of MFC systems. One way this can be achieved is by identifying economical and highly efficient anode, cathode and separator materials. For example, in a configuration that allows for a high SAV ratio (e.g., activated carbon granules) carbon could be an ideal material for the anode. Potentially, nanotechnology could be used to engineer ideal materials. Special consideration should be taken for the cathode material because most of the capital cost is concentrated here.^[72] Air-cathodes are one of the most promising strategies because they use the oxygen in the air as an electron acceptor. Along with inexpensive materials for current collection, diffusion layers, binders and catalysts, air-cathodes could become a viable option. Alternatively stainless steel mesh could be used as a current collector, polytetrafluoroethylene (PTFE) as an oxygen diffusion layer and PDMS as a binder, which can become a strong gas impermeable material under the correct plasma surface treatment.^[73] In fact, *Zhang et al.* successfully demonstrated the use of PDMS as binder in MFCs with comparable power generation and improved stability compared to Nafion and at a fraction of the price.^[74] Also, more economical alternatives for Pt as a catalyst could be CoTMPP, PbO₂ or MnO_x.^[75] Finally, the separator needs to deliver proton-transfer capability and long-term stability at a low cost. Improvements still need to be made from previous attempts where a low-cost, non-woven cloth presented low mechanical strength and a poor lifetime.^[76–77]

Furthermore, materials need to be stable over time, able to maintain biofilm electrochemical activity, reduce cathode deterioration and prevent fouling and separator deformation.^[56]

Costs may also be controlled and/or viability of MFCs increased at the commercial level if they are used in combination with other complementary technologies. For example, in addition to electricity generation during wastewater treatment, MFCs could be incorporated with other electrochemical reduction technologies that produce commercially valuable and energy-

rich chemicals such as ethanol, acetate, methane, hydrogen and hydrogen peroxide.^[78–79]

4.1. Applications

Figure 5. a) Second BMFC used to power buoy. Reprinted from ref. [80], Copyright 2008, with permission from Elsevier. b) Schematic of a sediment microbial fuel cell (SMFC) with power management system (PMS) used to operate a wireless sensor. Reprinted from ref. [82], Copyright 2011, with permission from Elsevier. c) MFC as toxicity biosensor [inset: Voltage response to introduction of toxic agent.] Reprinted from ref. [90], Copyright 2011, with permission from Elsevier.

There have been only few studies that show how it is possible to use the latest advancements of MFCs in real applications and diverse scenarios. Starting with a medium scale, in 2007, *Tender et al.* developed two benthic MFCs, where ocean sediment acts as the inoculum, the nutrient-rich anodic media and the proton-exchange membrane,^[80] with the aim of powering up a meteorological buoy. The first implemented cell was too costly, bulky and heavy with a volume of 1.3 m³, but was able to sustain 24 mW and successfully power up the buoy. The second cell was a lighter and cheaper design with a volume of 0.03 m³, and capable of powering the buoy with an out power of 36 mW

(Figure 5a).^[81] This successful project is a great example of the possibilities and potential of MFCs to operate and enable low-power sensors in long-term studies as practical, maintenance-free alternative to batteries.

Another successful experience was the sediment microbial fuel cell (SMFC) with a custom-designed power management system (PMS) developed by *Donovan et al.* Similarly to BMFCs, a SMFC generates current by the oxidation of sedimentary organic carbon and sulfur compounds by colonizing bacteria on a buried anode (Figure 5b).^[82] The PMS was then able to store energy from the SMFC in capacitors and use it in short bursts. Together, the system managed to power up a remote sensor consuming up to 2.5 W.^[83]

Similar approaches have been demonstrated ever since focusing mainly on the design of self-sustainable PMS,^[84] for example, including the use of ultracapacitors as an effective way to control power and voltage delivery to be able to drive a wireless temperature sensor.^[85]

Coming to the miniature scale, fewer studies have actually shown the usability of micro-sized MFCs under real scenarios and applications. An interesting approach has been proposed where MFCs can be used as biosensors to measure environmental parameters such as water toxicity or biochemical oxygen demand (BOD).^[86-89] Considering the fast start-up times of micro-sized MFCs, such sensors could be successfully implemented to achieve faster response times while preserving accuracy. In 2010, *Davila et al.* demonstrated a microfabricated MFC as biosensor for detection of toxic matter. The device consisted on two 144- μ L chambers with gold-coated silicon substrates as electrodes, incorporating a micro-patterned array of 300- μ m-deep channels and a proton exchange membrane between them. When any toxic compound is present in the anolyte solution, a drastic drop in current can be easily detected (Figure 5c).^[90] A possible improvement would be the optimization of the design to eliminate the need of a continuous flow of catholyte solution, which incurs in usage of additional energy.

5. Summary and outlook

Here, we present a summary of MFCs built using micro- and nano-fabrication techniques to optimize their power generation values. Micro-sized MFCs have the advantage of a fast start-up time, which allows them to rapidly test different components (such as materials, microbes, fuels and architectures) in a cell. Using microfabrication techniques, the SAV can be increased and the proton diffusion length decreased. Furthermore, microsystems that use laminar flow in microfluidic systems to separate the anode from the cathode in the absence of a proton-exchange membrane could be useful. In addition, arrays can be formed, although care needs to be taken to avoid voltage reversal effects and to reduce internal resistance, pressing concerns in any series system. Likewise, nanomaterials can be used to enlarge surface area and to provide easier, more direct access between microbes and electrodes for a more efficient transfer of electrons. In carbon nanotubes for example,

biocompatibility and efficient electrical conductivity conveys improved electrode performance to the MFC.

Table 1 summarizes the materials, bacteria and fuel used to build micro-sized MFCs and reports on the output and stability of each cell. A couple observations are immediately evident: a tight architecture that prevents oxygen intrusion will ultimately help to improve power generation (an added O₂ scavenger can also be helpful such as L-cysteine), and the large SAV provided by nanomaterials maintains an efficient connection between bacteria and anode, which maximizes the potential current.

Finally, we briefly overviewed a few points important to scaling up and the commercializing of MFC technology: optimizing power generation and management; reducing capital costs, including the selection of economical but highly efficient and long-term stable materials and the integration of MFCs with other technologies to complement functionality and add commercial value; and optimizing power density by increasing electrode surface area, particularly in the cathode, and by minimizing electrode separation, which also reduces the internal resistance of the cell.

At present, several pilot-scale MFCs demonstrate the potential for commercialization in the next few years. Large-scale operations were first demonstrated by the Advanced Water Management Center at the University of Queensland, Australia, with a 12-module, 1000 L MFC at a Foster's brewery. However, their design requires some improvements. For example, a build-up of excess of biofilm was present around the cathodes and the current was limited by low conductivity of the anode solution.^[17] Similarly, researchers at the University of Connecticut and collaborators showed a large-scale MFC with Pt-catalyzed carbon-cloth cathodes capable of removing 80% of the chemical oxygen demand present at concentrations of 300-600 mg L⁻¹.^[17, 91]

Further optimization and studies of micro-sized MFCs is also crucial in the development and implementation of scale-up applications since it can contribute with a better understanding on the fundamental phenomena that affect the final performance of the cell. Moreover, such studies can be performed in a fast and more efficient way than larger cells, due to their inherent higher mass flux density per unit area, which leads to faster start-up times. Additionally, their effective manufacturability goes along with the possibility of performing several studies in parallel as demonstrated by *Hou et al.*^[20] Nevertheless, it is imperative to recognize that diverse effects will impact any scale-up operation and therefore it is also fundamental to come up with effective and comprehensive mathematical and computational models, capable of delivering accurate estimates of the main operation conditions such power and efficiency, consequently also optimizing the design phase.

For the implementation of micro-sized MFCs as an efficient energy source to power microsystems, internal resistance must be optimized; borrowing strategies from other technologies, such as contact engineering, can be a powerful approach. Novel nanomaterials and microfabrication structures can also be effective. Future investigations aimed to improve the efficiency of micro-sized MFCs will reveal new and more electrochemically active strains of bacteria, optimal structural designs and

subsequently superior electrical performance. Moreover, this kind of miniature cells can be effectively used as biosensors or in lab-on-a-chip applications for diverse environmental condition detection such toxicity or BOD levels. Certainly, microfabricated

MFCs will continue to be an important part of the future development, success and ultimately the commercial distribution of MFCs.

Table 1. Comparison table between selected microfabricated MFCs.

Year	Ref.	Anode volume [μL]	SAV [cm^{-1}]	Electrode distance [μm] ^a	Anode			Membrane (Thickness [μm])	Cathode		Contact method	Power density [W/m^2]	Current density area [mA/m^2]	Duration [h]
					Substrate/Electrode	Bacteria	Fuel		Substrate/Electrode	Catholyte				
2003	Chiao et al. ^[26]	4	32 *	343	Si/Gold	Saccharomyces cerevisiae	Glucose + methylene blue	PEM (183)	Si/Gold	Ferricyanide	Aluminum foil on gold	0.5	294 *	1
2008	Siu & Chiao ^[27]	10	144	383	PDMS/ Gold	Saccharomyces cerevisiae	Human plasma	PEM (183)	Gold	Ferricyanide	Directly on gold pads	32.1 *	302	1
2009	Qian et al. ^[28]	1.5	100	283	Si/Gold	Shewanella oneidensis MR-1	Tryptic soy broth (TSB) / Sodium lactate	PEM (183)	PDMS/ Carbon Cloth	Ferricyanide	Wires from gold and CC	15.3	130 *	180
2011	Qian et al. ^[29]	4	100	183	PDMS/ Carbon Cloth	Shewanella oneidensis MR-2	Tryptic soy broth (TSB) / Sodium lactate	PEM (183)	PDMS/ Carbon Cloth	Ferricyanide	Directly from CC's	62.5	100 *	100
2011	Choi et al. ^[30]	4.5	500	490	Glass+ PDMS/ Gold	Geobacter-enriched mixed bacterial culture	Sodium acetate media + L-cysteine	CEM (450)	Glass/Gold	Ferricyanide	Copper on gold pads	2300	330	60
2013	Dai et al. ^[31]	140	0.05	-	PMMA/Gold	Shewanella oneidensis MR-1	L-broth media	PEM (183)	PMMA/Gold	Ferricyanide	Copper tape + silver paste on gold pads	2.65×10^{-4} *	23	7.5
2014	Ren et al. ^[32]	100	40 *	683 *	Glass/Gold	Geobacter-enriched mixed bacterial culture	Sodium acetate media [continuous]	PEM (183)	Glass/Gold	Ferricyanide	Copper foil on gold electrode	3300	2400	6+ [days]
Microfluidic														
2011	Li et al. ^[41]	0.3 ^b	117 *	200	Glass+ PDMS/ Gold	Geobacter sulfurreducens / Shewanella oneidensis MR-1	Acetate media / Lactate media	-	Glass/Gold	O ₂ saturated isotonic phosphate buffer	Copper soldered on gold	-	25.42	5 [days]
2013	Wang and Su ^[42]	0.36 *	208 *	1000	Glass+ PDMS/ Gold	Mixed culture	Acetate media	-	Glass/Gold	Aerated phosphate buffer	Directly from gold	-	-	1
Nanomaterials														
2012	Mink et al. ^[33]	1.25	~66000	233	Si/ MWCNT	Mixed culture	Acetate media	PEM (183)	PDMS/ Carbon Cloth	Ferricyanide	Copper wire on NiSi	392	197	50
2012	Inoue et al. ^[34]	40	-	4025	Si/CNT	Geobacter sulfurreducens	Acetate + fumarate media	PEM (25)	Si/Gold	Ferricyanide	Wires on metal pads	8.1 *	15.55 *	10
2013	Mink et al. ^[35]	75	~66000	3000	Si/ MWCNT	Mixed culture	Acetate media	-	Air cathode	-	Copper wire on NiSi	6.3 *	880	16 [days]
2014	Mink et al. ^[36]	25	10	1000	Copper/ Graphene	Mixed culture	Saliva	-	Air cathode	-	Directly from copper	6	1190 *	10 [days]
2015	Ren et al. ^[37]	12.5	40	678	Gold-coated glass / SS/LbL CNT	Geobacter-enriched mixed bacterial culture	Sodium acetate media [continuous]	PEM (178)	Glass/Gold	Ferricyanide	Copper foil on gold electrode	3320	2600	7 [days]

[*] Calculated from reported data. [a] Distance calculated including the thickness of the used membrane. [b] Volume reported for both anode and cathode.

Keywords: energy conversion • microfabrication • microbial fuel cell • nanotechnology • water treatment

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Entry for the Table of Contents

REVIEW

In this review, we summarize some of the recent efforts using microfabrication techniques to build micro-sized cells, and we elaborate on their advantages and challenges. Finally, we discuss integration of nanomaterials into MFCs and end with key considerations for scaling-up, commercialization and some applications.

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Muhammad M. Hussain**

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**The Role of Microfabrication and
Nanotechnology in the Development
of Microbial Fuel Cells**