
Microfluidics in Membraneless Fuel Cells

Jesus A. Diaz-Real, Minerva Guerra-Balcázar, Noe Arjona,
Francisco Cuevas-Muñiz, Luis Gerardo Arriaga and Janet Ledesma-García

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Abstract

In the 1990s, the idea of developing miniaturized devices that integrate functions other than what normally are carried out at the laboratory level was conceived, and the so-called “lab-on-a-chip” (LOC) devices emerged as one of the most important research areas. LOC devices exhibit advantages related to the use of microfluidic channels such as small sample and reagent consumption, portability, low-power consumption, laminar flow, and higher surface area/volume ratio that enhances both thermal dissipation and electrochemical kinetics. Fuel cells are electrochemical devices that convert chemical energy to electrical energy. These are considered as one of the greener ways to generate electricity because typical fuel cells produce water and heat as the main reaction byproducts. The technical challenges to develop systems at the microscale and the advantages of microfluidics exhibited an important impact on fuel cells for several reasons, mainly related to avoid inherent problems of gaseous-based fuel cells. As a result, the birth of a new type of fuel cells as microfluidic fuel cells (MFCs) took place. The first microfluidic fuel cell was reported in 2002. This MFC was operated with liquid fuel/oxidant and had the advantage of the low laminar flow generated using a “Y” microfluidic channel to separate the anodic and cathodic streams, resulting in an energy conversion device that did not require a physical barrier to separate both streams. This electrochemical system originated a specific type of MFCs categorized as membraneless also called colaminar microfluidic fuel cells. Since that year, numerous works focused on the nature of fuels, oxidants and anodic/cathodic electrocatalysts, and cell designs have been reported. The limiting parameters of this kind of devices toward their use in portable applications are related to their low cell performances, small mass activity, and partial selectivity/durability of electrocatalysts. On the other hand, it has been observed that the cell design has a high effect on the cell performance due to internal cell resistances and the crossover effect. Furthermore, current technology is growing faster than last centuries and new microfabrication technologies are always emerging, allowing the development of smaller and more powerful microfluidic energy devices. In this chapter, the application of microfluidics in membraneless fuel cells is addressed in terms of evolution of cell designs of miniaturized microfluidic fuel cells as a result of new discoveries in microfabrication technology and the use of several fuels and electrocatalysts for specific and selective applications.

Keywords: energy conversion systems, lab-on-a-chip, membraneless, microfluidic fuel cells

1. Introduction

1.1. Microfluidic fuel cells: concept, classification, and challenges

In 1989, R. Howe introduced the term “microelectromechanical systems” (MEMS) to describe a research field in which the machining was below the millimeter scale [1]. The rapid growth in the following years in this area generated several branches in electronics, including power sources technologies where fuel cells were comprised. However, hydrogen as the fuel for the supply of these miniaturized devices results very dangerously in the gas form and makes it complicated to store as liquid. Therefore, the use of hydrogen-containing liquid fuels such as alcohols became more attractive for portable applications due to their ease of storage and high-mass energy density (6.1 kWh/kg) [2]. The integration of these elements into the fuel cells introduced an important characteristic that well defines the operating principle of a microfluidic fuel cell (MFC).

Typically, an MFC is a fuel cell that operates with two liquids (one fuel and the other oxidant) that are introduced by a mechanical mean into a single microchannel at laminar flow (low Reynolds number) to establish an interface. The fuel and oxidant stream will be in contact with an anodic or a cathodic surface, respectively. Both parallel streams allow the continuous flow through the length of the channel without mixing and preventing possible fuel crossover. The low speed allows the diffusion of protons between the streams in order to perform the electrochemical processes, which replaces the proton-exchange membrane (PEM) [3]. From its first appearance in 2002 to the present day, several architectures regarding the shape of the channel, electrodes geometric arrangement, oxidant supply source, and fuels have been studied. It is also common to refer MFC as laminar flow fuel cells (LFFCs) in literature indistinctively.

1.2. Microfluidic fuel cell categories

With the recent development of MFCs, a subcategory has been created to include all these membraneless cells. Generally, fuel cells have been classified by the membrane used such as polymer electrolyte fuel cells (PEFCs), solid-oxide fuel cells (SOFCs), and others. In the case of the MFCs, two main aspects have been used to classify them and are based either on the physical phases in which fuel and oxidant streams are found [4] or the stream delivery mode onto the electrodic surface [5].

1.2.1. Liquid fuel/liquid oxidant

The first categorization distinguishes reactants in liquid phase. Several fuels have been studied, including alcohols (methanol and ethanol mainly) [6–9], formic acid [10–14], glycerol [15], glucose [16, 17], dissolved hydrogen [18], V^{+2} [19, 20], among others. It is common to see the use of dissolved oxygen as the oxidant phase [10, 12, 21, 22], while the same is not true in the case of H_2O_2 [23, 24], VO_2 [19, 25, 26], and $KMnO_4$ [25, 27, 28]. An important advantage is the wide range of pH supported by this type of MFCs since the membrane is not the limiting issue. This allows the choice of supporting electrolyte to tailor the optimal operating conditions for

the electrodic materials. However, a major issue in these systems is the sudden formation of bubbles due to the gas byproducts (namely, CO_2) that lead to the drop of ionic conductivity, perturbation of the colaminar interface, streams crossover, or even channel blockage [4].

1.2.2. *Liquid fuel/gas oxidant*

Oxygen is by far the most used, easily available, and low-cost oxidant for MFCs. It is well known that slow kinetics of oxygen reduction (cathodic side) greatly determine the efficiency of fuel cells and the same problem affects MFCs. To address this problematic issue, Jayashree et al. innovated an MFC by introducing the concept of an air-breathing cathode that enhanced the performance of this electrode since oxygen diffusion coefficient is four orders of magnitude higher in air than in an aqueous solution [29]. This opens the opportunity to hypothetically expand this idea to many other cells because the need of both streams is still necessary to form the colaminar interface. However, several considerations are needed to take into account during the implementation of air-breathing electrodes. Air access, atmospheric counterpressure, and drying rate in bigger electrode areas are some of the parameters that might affect the performance of these MFCs when they are scaled up.

1.2.3. *Flow-over stream*

One of the simplest models of MFCs involves the two distributions of the electrodes, as depicted in Figure 1: (a) a parallel arrangement (facing up or over the walls) with a vertical colaminar diffusion interface and (b) facing each (top-bottom) other with a horizontal interface. In the first case, reorientation of the interface induced by gravity is possible when there is an important difference in the densities of the streams, while for the configuration with a horizontal interface this issue is more evident, increasing the crossover stream rate [30]. Regardless of the crossover problem, the amount of electrolyte that is reacting and in intimate contact with the electrodic surface is limited to the geometry of the electrode and to the flow speed. This is due to the planar electrode configuration, and thus, only the adjacent fraction of the streams is available to react. Then, the local reactant concentration will decrease while the generated subproducts will increase. This situation, along with the low convective flow speed, will generate a depletion layer near the electrode surface and a gradient of reactant concentration. Therefore, the utilization of the electrolyte is minimal, which demands an improvement in the cell design to enhance the fuel utilization [5].

1.2.4. *Flow through stream*

Considering the issue on electrolyte utilization, three-dimensional porous structures for electrodes were proposed. This configuration makes use of the entry of the electrolyte through the electrode itself, forcing the intimate contact to maximize the reactant consumption by rapid convective transport, replenishing the species. Another name used to refer to this configuration is multiple inlets, and the term was first proposed by Kjeang et al. [31]. An MFC with carbon paper porous electrodes was reported by Salloum et al. that used formic acid as the fuel [27].

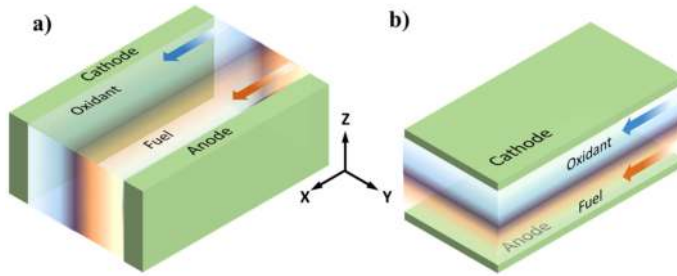


Figure 1. Schematic image of the overflow designs: (a) top-bottom electrode configuration and (b) side-by-side parallel configuration. The darker color shows the diffusion interface, while a transparent color shows the depletion layer near the electrode surface.

One important challenge that faces this type of electrodes is the electrocatalyst deposition. Since the porosities of the electrode are in a smaller scale, the classical paint-spray deposition technique cannot ensure a homogeneous dispersion in the inner electrode area. Hence, new techniques for electrode preparation needs to be further investigated.

2. Thermodynamic and kinetic of microfluidic fuel cells

Microfluidics is a research field in which the studied phenomena occurs in confined structures with a characteristic dimension within 1–1000 μm [32]. At this scale, low Reynolds numbers yielding laminar flows facilitate characterization of the fluid mechanics. Therefore, viscous and capillary forces, rather than volumetric or gravitational effects, govern these systems more importantly. The behavior of the fluids in the microchannels allows us to consider them as a continuum, and thus, we can follow the continuity equation for mass conservation for a fluid in Eq. (1)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0 \quad (1)$$

If the density of the fluid remains constant, the equation is simplified by the condition of incompressible flow, $\nabla \cdot \vec{u} = 0$. Then, the Navier-Stokes equation is valid to describe the velocity field, \vec{u} :

$$\rho \left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \nabla \cdot \vec{u} \right) = -\nabla p + \mu \nabla^2 \vec{u} + \vec{f} \quad (2)$$

with p being the pressure and \vec{f} a term summarizing all body forces per unit volume.

Since the main difference between PEMFC and MFC systems relies on the replacement a physical membrane with the liquid-liquid interface, their electrochemical operating principles remain almost identical. Due to the large amount of reports making use of organic molecules as fuel, it is convenient to remind the fundamentals of direct alcohols fuel cells (DAFC) [33]. For the sake of understanding the thermodynamics of their process, we will use CH₃OH electrooxidation on a Pt surface in acid media as an example. CH₃OH can be directly oxidized to carbon dioxide, although other subproducts (namely, formaldehyde, formic acid, etc.) can be produced depending on the reaction pathway.

In an assembled MFC, two reactions occur: (1) the fuel oxidation in the anode side and (2) the electroreduction of the oxidant (oxygen, for an example) at the cathode side. The general overall reaction is presented below:

| | | | |
|----------------------|---|---------------------------------------|----------|
| Fuel/anode side | $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ | $E_{298}^\circ = 0.04 \text{ V/SHE}$ | (Rxn. 1) |
| Oxidant/cathode side | $3/2\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 3\text{H}_2\text{O}$ | $E_{298}^\circ = 1.229 \text{ V/SHE}$ | (Rxn. 2) |
| Overall | $\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ | | (Rxn. 3) |

The overall reaction potential can be obtained by the subtraction of the anodic thermodynamic potential reaction to the cathodic value, $E_c - E_a = E_{\text{cell}} = 1.19 \text{ V}$. This process has an associated thermodynamic efficiency that can be calculated by obtaining the ratio of Gibbs free energy (the maximum electrical work of the system, ΔG°) between the enthalpy (the total available energy, ΔH°),

$$\varepsilon_{\text{eq}}^{\text{rev}} = -\Delta G^\circ / -\Delta H^\circ \quad (3)$$

Methanol has a theoretical enthalpy of combustion of -715 kJ/mol [34]. With the standard electromotive force equation, it is possible to calculate the ΔG° at equilibrium

$$\Delta G^\circ = -nF \times E_{\text{eq}}^\circ = -6 \times 96,485 \times 1.19 = -688.9 \text{ kJ / mol} \quad (4)$$

where F is the Faraday constant ($96,485 \text{ C/mol}$) and n is the number of exchanged electrons for the electrooxidation of CH₃OH. Then, the theoretical efficiency of the system is given by Eq. (5):

$$\varepsilon_{\text{eq}}^{\text{rev}} = -\Delta G^\circ / -\Delta H^\circ = 688.9 / 715 = 96.3\% \quad (5)$$

In a real experimentation, the formation of intermediates and subproducts determines in great measure the performance of the cell. These species depend on associated factors, but not limited to the reactive surface, catalyst composition, crystalline structure, and electrode

potential. Other conditions, such as pH, electrolyte temperature, fuel concentration, and reaction time/flow speed, also have to be considered [35].

The differences encountered between the theoretical and actual values for E_{cell} are usually addressed to three limiting factors: (1) charge transfer overpotentials (η_{act}) in either the anodic or cathodic catalyst due to slow kinetics, (2) the ohmic drop ($R_e j$, resulting from the product of the electrolyte resistance, R_e , and the recorded current density, j), and (3) mass transfer constrains [33]. Adding these new terms to the E_{cell} equation, the resulting expression is Eq. (6):

$$E_{\text{cell}} = E_{\text{eq}}^{\circ} - \eta_a - \eta_c - R_e j \quad (6)$$

With η_a being the anode overpotential and η_c the cathode overpotential, this equation considers both kinetic and mass transfer limitations. As previously mentioned, the specific reaction pathway might lead to incomplete fuel oxidation, and thus, the reaction will have a different number of exchanged electrons, n_{real} . If these considerations are included to the cell efficiency expression, we have Eq. (7):

$$\begin{aligned} \varepsilon_{\text{cell}}^{\text{CH}_3\text{OH}/\text{O}_2} &= -\frac{n F E_{\text{cell}}}{\Delta H^{\circ}} = -\left(\frac{n_{\text{real}} F}{\Delta H^{\circ}}\right) \left(\frac{n}{n}\right) \left(\frac{E_{\text{eq}}^{\circ}}{E_{\text{eq}}^{\circ}}\right) = \\ &= \left(\frac{n_{\text{real}}}{n}\right) \left(\frac{E_{\text{cell}}}{E_{\text{eq}}^{\circ}}\right) \left(\frac{\Delta G^{\circ}}{\Delta H^{\circ}}\right) = \varepsilon_F \varepsilon_E \varepsilon_{\text{eq}}^{\text{rev}} \end{aligned} \quad (7)$$

where ε_F is related to oxidation reaction efficiency and ε_E involves the kinetics and ohmic drop limitations. From this last expression, it is easy to understand that the only possible way to improve the cell efficiency is by decreasing the overpotentials and/or ohmic drop, and promoting the complete fuel oxidation [34].

For the ohmic loss, a factor that primarily contributes is the electrode separation (d) and the geometric exposed area (A). Thus, by increasing the ratio, A/d , ohmic losses are minimized. Nevertheless, ionic force in the electrolyte is significant to ohmic drop, and increasing the concentration of the supporting electrolyte reduces its negative impact. Mass transfer limitations are related to the availability of the species over the electrodic area. Then, the main issues are presented in the electrode vicinity due to the low concentrations as a consequence of the consumption of reactant species, which leads to the thickening of a depletion layer. This layer becomes a limiting mass transfer factor when fresh reactants are not efficiently replenished on the reactive surface, mainly due to slow flow rates [5]. The distributions of the species concentration are controlled by convective (stream flow) and diffusive (concentration gradient) transport, which are described by the mass conservation equation in Eq. (8):

$$\nabla \cdot (-D_i \nabla C_i + C_i \vec{u}) = S_i \quad (8)$$

with D_i the diffusion coefficient for the specie “ i ,” i being either the fuel or oxidant depending on the cell compartment, C_i the concentration of the specie “ i ,” and S_i the volumetric net rate of consumption for the specie “ i ” due to its corresponding electrochemical (oxidation or reduction) reaction. Then, S_i is estimated directly by the current density (i) obtained from the corresponding electrochemical reaction and given by the Butler-Volmer in Eq. (9):

$$S_i = \frac{i}{nF} = \frac{i_0}{nF} \left(\frac{C_i}{C_i^*} \right) \left[e^{\alpha_a f \eta} - e^{\alpha_c f \eta} \right] \quad (9)$$

where i_0 is the exchange current, C_i^* is the bulk concentration of specie i , α_a and α_c are the charge transfer coefficients for anodic and cathodic reactions, and η is the electrode overpotential. Since S_i depends on convective effects, the efficiency of the cell can be determined dividing by the flow rate:

$$\varepsilon_{fuel} = \frac{i}{nFv} \quad (10)$$

where ε_{fuel} is the fuel efficiency utilization and v is the fuel flow rate. Hence, higher flow speeds will supply the electrodes with electrolyte at the initial concentration preventing the increase of products in the depletion layer but decreasing ε_{fuel} .

3. Evolution of microfluidic fuel cell designs

The evolution of the microfluidic fuel cell is related to the pursuit of more power in less volume. Many factors have been considered including size, weight, physical resistance, and lifetime [14, 21]. Lightweight structural materials are preferred such as polymethyl methacrylate (PMMA) and poly-dimethylsiloxane (PDMS) [13, 14, 21, 36]. Moreover, UV-sensitive resists, such as SU-8, have demonstrated to be excellent candidates to build MFC pieces since they present some important advantages like the flexibility and capability to be sealed to each other by a hot-pressing technique [37].

3.1. Microfabrication techniques

In order to obtain more energy in the same volume, more sophisticated micromachining techniques have been employed. Some techniques even employ clean room facilities. The principal considerations for the choice of one or another micromachining technique are the selection of the structural material, the size of the microstructures, and the complexity of the structures. The polymers can be machined by Xerography, micromolding, hot embossing, and micromilling. In addition, assisted-laser techniques can be employed including photolithography, laser ablation, or stereolithography.

Micromilling is a very simple technique performed with a CNC micromilling cutter, useful for rigid polymers (i.e., PMMA). Micromilling is limited by the size of the cutter, it is uncommon to find below the 1/64 and often very fragile. Also, flexible polymers cannot be machined using this technique.

Xurography is a fast and low-cost process. It uses a plotter cutter to draw the channels in a protective mask placed over the substrate, later a conductive layer is placed over the substrate. Finally, the mask is removed leaving the conductive layer printed in the substrate. This technique is especially useful for electrodes and microchannels [38] (see Figure 2).

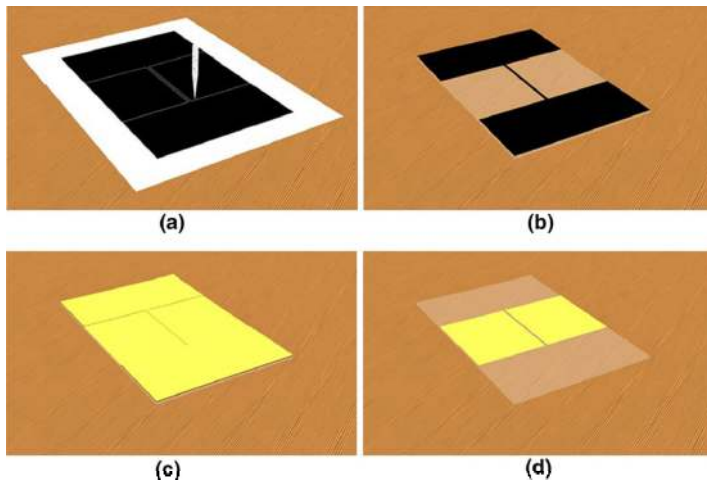


Figure 2. Schematics for electrodes on glass process flow based on xurography technique. (a) Patterning of vinyl film (xurography). (b) Removing of film and transfer on glass slide surface. (c) 30 nm Cr and 300 nm Au deposition. (d) Removing of film (dry liftoff) (taken from [39]).

Micromolding and hot embossing are similar techniques. A mold is used, however in micromolding a liquid resin is placed in a mold with the desired shape and is dried at room temperature by heat. In hot embossing, a solid polymer is heated to soften the material and then thermoformed by heat and pressure. Usually, these kinds of techniques are popular because of their simplicity. In both cases, the mold fabrication can be performed by micromilling or a laser technique.

Laser is a versatile tool for the construction of microstructures. Laser is used with a positive or a negative photoresin in order to obtain the desired pattern in the polymer. Laser techniques require the use of a clean room. In the photolithography, a UV laser beam is used to draw a pattern in a positive photoresin, generally a photoresist mask is used to protect the UV-sensitive material. Later, the sample is washed in order to remove the residues. Other alternative is the fabrication of a mold in negative photoresin, and later performed the casting of a polymer shell, as PDMS [13].

The technique of laser ablation allows drawing a microchannel from inside of a transparent polymer. A nanosecond or femtosecond pulsed laser is used to generate a three-dimensional pattern since the interior of material avoiding the need to paste several layers in the same piece (Figure 3) [39].

Stereolithography (SLA) is an additive technique (Figure 3). A negative photoresin (as SU-8) is placed over the support and cured with a laser beam, making a solid polymer with the desired structure. The main disadvantage of this procedure is the high cost of the machine (several hundred of dollars) [40].

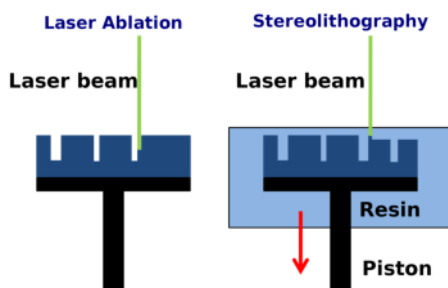


Figure 3. Destructive (laser ablation) and constructive (stereolithography): two different principles of microfabrication techniques. In ablation, the substrate is destroyed in order to obtain the pattern. In the stereolithography, the substrate is formed.

3.2. Microfluidic fuel cells two-dimensional electrode

We have seen a fuel cell evolution through the exhaustive analysis of literatures concerning membraneless MFCs. This evolution can be summarized at five principal stages:

- a. Close cells where both streams (anodic/cathodic) flow over electrodes.
- b. Open cells where both streams flow over electrodes.
- c. Open cells with an anodic stream flowing through the electrode.
- d. Close cells where both streams flow through electrodes.
- e. Open cells where both streams flow through electrodes.

The one and two stages correspond to microfluidic systems in which the anodic and cathodic streams are only in contact with the electrode surface (long and wide, Figure 4, delimited by blue arrows). The reason of this design is to consider membraneless MFCs with two-dimensional electrodes. In addition, because of fuel and oxidant flow laterally to electrodes, these are called as MFCs with flow-over electrodes. All devices that operate under this condition (lateral flow) and use small organic molecules (i.e., formic acid, methanol, ethanol, glycerol, etc.) as fuels and oxygen as oxidant have shown low-power densities, where an important limiting factor is the reduced geometrical area. With this in mind, plenty of investigations have

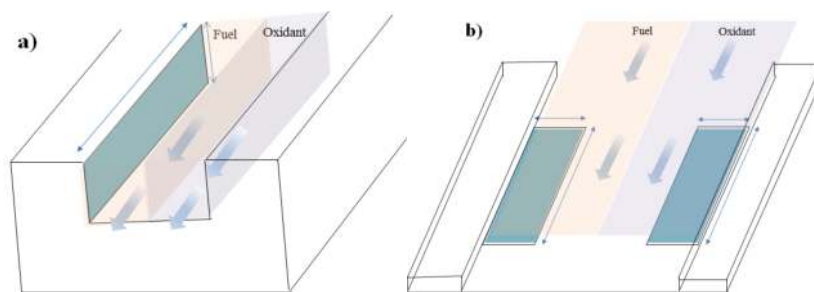


Figure 4. Contact area of fuel and oxidant streams in membraneless microfluidic fuel cells with two-dimensional electrodes: (a) “Y”-type with electrodes on channel walls [19] and (b) “Y” type with electrodes on channel floor [13].

been focused to increase the activity through enhancing the cell design, and others using supports with high surface area of different nature, such as carbon nanotubes [14, 15] and polyaniline [41]. These supports also enhance the reaction due to the improvement of electron transfer, modifying the metal-support interactions. The low concentration and diffusivity of oxygen in solution are another important parameter that limits the power density of membraneless MFCs [10]. For this reason, the two-dimensional electrode MFC has been slightly modified using porous air-breathing cathodes (Figure 5). Hence, it profits from the oxygen in air that has 10,000-fold higher diffusivity than in aqueous solution. Also, the oxygen concentration in air is higher (10 mM) than in solution (2–4 mM) [29].

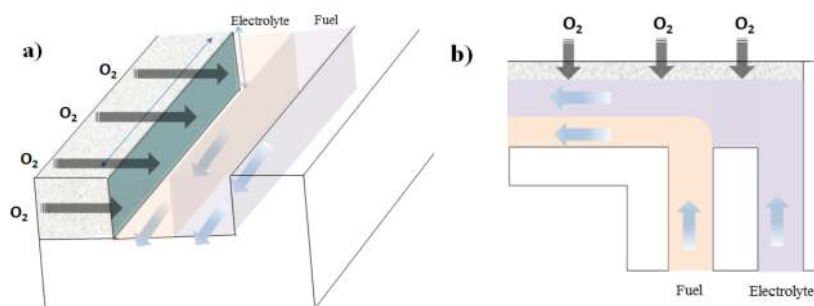


Figure 5. Membraneless microfluidic fuel cell with porous cathode as flow-over electrode: (a) typical “Y” and “T”-like configuration and (b) “F”-like channel configuration.

3.3. Microfluidic fuel cells three-dimensional electrode

Another strategy to enhance the power density is related to the increase of the contact area between the electrocatalyst and electrocatalytic solution. Carbon paper as porous electrode has been used as diffuser in proton exchange membrane (PEM) fuel for cells many years before the first membraneless MFC was reported [42–45]. Kjeang et al. have explored the use of these

porous carbon electrodes in MFC, where fuel and oxidant are circulating through them, emerging the term of “MFCs with flow through electrodes” or “three-dimensional electrode MFCs” (Figure 6) [31, 46]. These devices benefit from the high surface area of carbon paper ($230 \text{ m}^2 \text{ g}^{-1}$) and carbon nanofoam ($450 \text{ m}^2 \text{ g}^{-1}$) to enhance the cell performance.

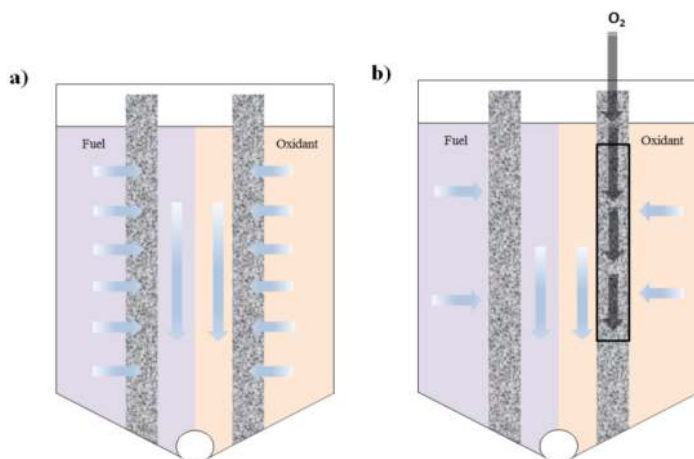


Figure 6. (a) Schematic representation of membraneless microfluidic fuel cell with flow through electrodes and (b) with air-breathing window [48, 49].

The modifications of membraneless microfluidic fuel cells between flow-over electrodes and flow through electrodes as well as the use of air as oxygen source have resulted in enhancement of the cell performance. Figure 7 illustrates the evolution of these devices by changes in contact areas as discussed earlier. Changes were observed in the current density as a function of the MFC stage. The range in the stage: (i) is in the order of $8\text{--}12 \text{ mA cm}^{-2}$ and (ii) it depends on the utilized fuel. The use of porous material as the oxygen source (stage ii) in an air breathing resulted in current densities from 15 to 130 mA cm^{-2} . The use of a flow through anode (stage iii) increases the current density up to 140 mA cm^{-2} . In the case of an MFC, which works with a flow through anode and cathode, formic acid as fuel and oxygen-saturated solution as oxidant, the reported current density was of 20 mA cm^{-2} (stage iv)) [47].

When the MFC with flow-through electrodes combines oxygen from air and from an oxygenated solution, the current density increases to values up to 100 mA cm^{-2} as tested for different fuels [48]. In the case of formic acid, current density of almost 500 mA cm^{-2} has been reported [49]. As summary, the performance of membraneless MFCs has shown high dependence on the way that the fuel and oxidant streams flow in the anode and cathode as well as with strategies to increase/enhance the oxygen source. The use of electrodes with higher surface areas as flow-through electrodes can be considered as an important alternative to improve the cell performance of this kind of devices, which could allow them for use as power supplier for small devices such as cellphones, cameras, etc.

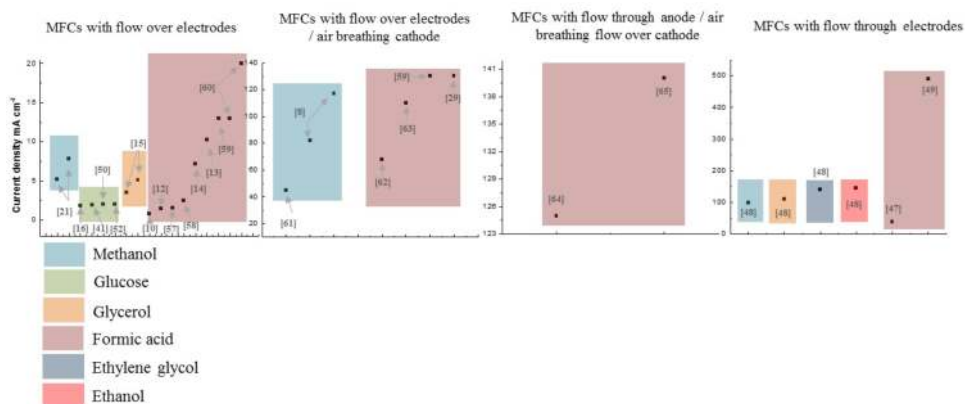


Figure 7. Current density evolution on single membraneless microfluidic fuel cells, which employ small organic molecules as fuel as function of contact form of fuel and oxidant streams to electrode surfaces (references used are listed from left to right) [21, 16, 51, 52, 12, 53, 54, 13, 55–57, 8, 58–61].

4. Fuels and performance evolution

Several research groups have worked on the development of such energy conversion devices that operate on various fuels such as glycerol, ethylene glycol, formic acid, glucose, ethanol, and methanol. Many designs have been optimized, as well as manufacturing techniques incorporating computational tools for modeling and construction photolithography equipment and numerical control systems, high-resolution components and electronic interconnect assembly, and development of electrocatalytic anodic and cathodic materials of inorganic and enzymatic nature.

In this context, we highlight the bimetallic core-shell materials (core-shell) used as anodes and cathodes for the oxidation of various fuels and the reduction of oxygen, respectively. For example, AuAg supported on nanoparticulated carbon was used for glucose electrooxidation in alkaline media [16, 50]. AuAg/C exhibited good stability, higher current density, and more negative anodic potential (ca. 150 mV) associated with this reaction than that achieved with bare Au supported on Vulcan. The performance of AuAg/C and Au/C was evaluated in a glucose laminar membraneless microfluidic fuel cell where the incorporation of Ag in the electrocatalyst contributed to increasing the AuAg/C activity using low Au loading.

With regard to recent development of cathodic electrocatalytic materials, stand-up PtAg/C alloys were employed for the oxygen reduction reaction (ORR). High selectivity for ORR was observed in the presence of glucose (100 mM) in basic media [51]. This result allowed the use of these bimetallic materials as cathode in an MFC that used glucose as fuel with an additional advantage arising from the use of less noble metal and less expensive material such as silver.

The combination of high selectivity of PtAg/C in the ORR and AuAg/C in the glucose oxidation reaction allowed the construction and evaluation of a glucose MFC with outstanding per-

formance at zero flow condition [52]. MFC was also evaluated with a simulated body fluid solution that contained salts commonly present in the human blood plasma, reaching a power of 240 mW cm^{-2} at zero flow. These results envisage the incorporation of this MFC as a portable power source in lab-on-a-chip devices without the need of external pumps.

Dector and coworkers developed a small air-breathing hybrid MFC using glucose from human serum and blood as a fuel with O_2 supplied from air [53]. This device showed an excellent performance (200 mW cm^{-2}) and good stability with potential applications as power source for use in building implantable and portable biomedical devices.

A new concept of membraneless air-breathing nanofluidic fuel cells with flow-through electrodes that can be powered by several fuels (individually or mixed) in alkaline media (i.e., methanol, ethanol, glycerol, and ethylene glycol) was recently reported [48]. A novel Cu@Pd core-shell electrocatalyst synthesized by chemical method revealed morphologies of nanorods particles of 10 nm in length and a typical semispherical particle with a diameter of 6 nm. The electrocatalytic properties of the rod/semispherical Cu@Pd nanoparticles supported on Vulcan carbon showed higher activity than commercial Pd/C in the electro-oxidation of each fuel and the mixture of them. The air-breathing nanofluidic fuel cells constructed with Cu@Pd/C anode exhibited individual power densities and current densities higher than 16 mW cm^{-2} and 100 mA cm^{-2} , respectively. A mixture of four fuels resulted in a voltage of 0.61 V with current and power densities of 108 mA cm^{-2} and 18 mW cm^{-2} , respectively. The reported devices displayed a better performance than current state-of-the-art systems and demonstrated the feasibility of developing multiuse nanodevices that provide constant power regardless of the fuel employed.

Finally, ethylene glycol has been used as fuel in PEM (polymer exchange membrane) fuel cells operating at temperatures ranging from 60 to 130°C [54, 55]. In microfluidic fuel cells, the use of ethylene glycol (EG) as well as glycerol has been sparse, and it could be related to the low performance by activity problems of electrocatalysts that are still found in PEM fuel cells. Arjona et al. [56] published, for the first time, the use of ethylene glycol in a membraneless MFC with lateral flow. In this work, a metal mixture of AuPd supported on polyaniline was used as anode. The performance device was tested as a function of EG concentration showing a maximum performance at 2 M EG and room temperature. A cell voltage of 0.53 V and a maximum current and power density of 14.2 mA cm^{-2} and 1.6 mW cm^{-2} , respectively, were achieved using oxygen from a saturated solution. The resulting cell voltage was comparable with those values reported for PEM fuel cells (0.4–0.65 V), which operate at higher temperatures ($60\text{--}90^\circ\text{C}$) [54, 55]. The finding was attributed to the enhancement in the electronic properties by the metal-metal AuPd interactions as well as the effect of polyaniline, which could enhance the metal/support interactions.

5. Conclusions and perspectives

Many reports published in the last decades have contributed to several findings in the MFC technological area. As discussed, numerous issues relevant to MFCs need further investigation and optimization.

The current trend is to develop devices that combine all three properties: power generation, energy storage, and electronic interface for a specific application. These three functions integrated in a single device with a dimension in the micro- or nanometrics have placed the technology in the category of lab-on-a-chip.

Some limiting conditions, such as potential drop and ohmic resistance, have been observed in the assembly of these MFCs. All electrical contacts and external circuit wiring are necessary to be optimized in order to reduce their impact on the MFC performance. The new machining technologies, such as three-dimensional printing, offer a precise and accurate option to develop the cell assembly parts.

In terms of electrochemistry, charge transfer is also a problem that affects many systems to date. These phenomena can be studied by properly implementing a reference electrode to provide a more detailed insight into the electrochemical processes occurring in each compartment. The sluggish kinetics is usually related to the electrocatalytic material and proper pH selection. However, temperature, fuel concentration, and other physicochemical parameters are factors to investigate with each new emerging cell design.

The development of these devices involves a multidisciplinary task in electrochemistry, nanotechnology, electronics, physics, mathematics, mechanical engineering, computer sciences, biotechnology, biomedical, and environmental engineering.

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Author details

Jesus A. Diaz-Real¹, Minerva Guerra-Balcázar², Noe Arjona¹, Francisco Cuevas-Muñiz¹, Luis Gerardo Arriaga¹ and Janet Ledesma-García^{1*}

*Address all correspondence to: janet.ledesma@uaq.mx

1 Center Research and Technological Development in Electrochemistry, Parque Tecnológico Queretaro Sanfandila, Queretaro, Mexico

2 Division of Research and Postgraduate, Facultad de Ingeniería, Universidad Autónoma de Queretaro, Cerro de las Campanas, Queretaro, Mexico

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