

# Abiotic, Hybrid, and Biological Electrocatalytic Materials Applied in Microfluidic Fuel Cells: A Comprehensive Review

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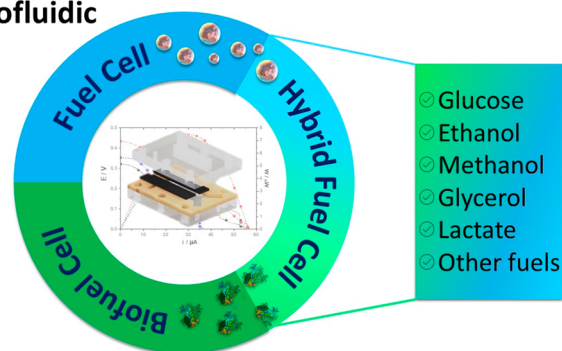
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**ABSTRACT:** This article provides an overview of the work reported in the past decade in the field of microfluidic fuel cells. To develop appropriate research, the most commonly used electrocatalytic materials were considered and a new classification was proposed based on their nature: abiotic, hybrid, or biological. This classification allowed the authors to discern the information collected. In this sense, the types of electrocatalysts used for the oxidation of the most common fuels in different environments, such as glucose, ethanol, methanol, glycerol, and lactate, were presented. There are several phenomena presented in this article. This information gives an overview of where research is heading in the field of materials for electrocatalysis, regardless of the fuel used in the microfluidic fuel cell: the synthesis of abiotic and biological materials to obtain hybrid materials that allow the use of the best properties of each material.

**KEYWORDS:** *microfluidic fuel cells, abiotic electrocatalyst, hybrid electrocatalyst, biological electrocatalyst, alternative fuels, glucose, ethanol, methanol, glycerol, lactate*

## Microfluidic



## INTRODUCTION

There are currently many problems to solve in the energy sector, but replacing fossil fuels with more environmentally friendly alternatives is a priority. The conversion of chemical energy into electrical energy is now a widespread practice using different fuels such as methanol, glycerol, glucose, or lactate as well as different types of electrocatalytic electrodes: abiotic, biological, or hybrid.

In this context, different configurations of fuel cells (FCs) have been tested with the main objective of achieving optimal power to perform everyday tasks. Nevertheless, these technologies have multiple limitations, especially in terms of cost.

A FC is an electrochemical device that produces a certain amount of electricity when the oxidation and reduction reactions take place in two different electrodes. An electrolyte is required between the electrodes to create an electrically isolated and ionically conductive environment.<sup>1,2</sup>

There are several architectures that determine the configuration for anolyte and catholyte flow through the microfluidic fuel cell. In the electrode configuration (where the electrocatalyst materials are deposited), the fuel flows between and reacts with the electrodes made of porous materials before

combining in a laminar flow; this architecture is called a “laminar flow” or microfluidic fuel cell.<sup>3</sup>

Laminar flow-based fuel cells are defined as devices that combine all of the components of a fuel cell in a single microfluidic channel and its walls and operate with a virtual membrane created by a laminar flow that maintains a separation between the fuel flow and the oxidant stream (Figure 1).

These operating principles of microfluidic devices allow versatility in design and practicality. Catalysts such as enzymes have adapted quite well to these technologies because of the need for a lower catalyst charge, lower amount of fluid, fuel option, and fluid mechanics phenomena that occur in these systems in addition to their application according to their voltage and output power generated.

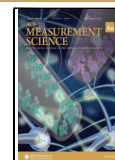
This work focuses on a specific type of fuel cell, defined as microfluidic fuel cells ( $\mu$ FC), which can deliver different

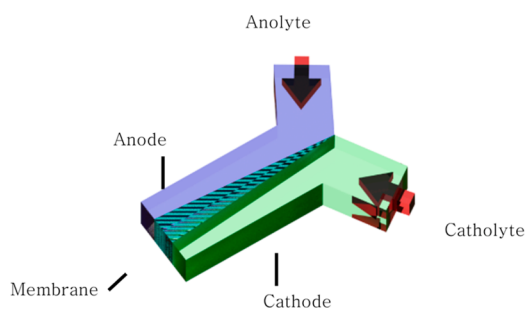
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**Figure 1.** Schematic representation of laminar flow in a microfluidic fuel cell.

amounts of energy depending on the reactions taking place in the device. The classification of microfluidic channels can vary depending on the author, but a diameter in the range from 10 to 200  $\mu\text{m}$  is generally accepted for microchannels.<sup>4</sup>

In this context, several authors have reported the advantages of their devices, such as a high surface-to-volume ratio, an economic aspect indicating a low-cost fabrication process, room temperature, and no additional humidity systems needed.

There are certain parameters that must be considered when designing and modeling a  $\mu\text{FC}$ , such as size, weight, volume at desired performance, temperature, humidity, fuel, and oxidant pressure.

Due to the advances in recent years and the enormous variety of materials and fuels used in this type of device, there is also a need to classify the electrocatalytic surfaces used in  $\mu\text{FC}$ , which is the main contribution of this work.

### ■ CLASSIFICATION OF MICROFLUIDIC FUEL CELLS

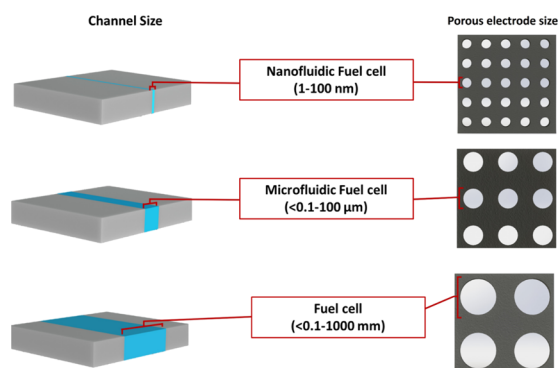
Microfluidic fuel cells ( $\mu\text{FC}$ ) have evolved their configurations and properties in recent years depending on the reactive species, flow configurations, electrode structures, and innovations.<sup>5</sup> The present work expands the spectrum of fuel cell classification by considering not only the microfluidic design but also a classification for fuel cells depending on the type of electrocatalytic electrode used for fuel oxidation: abiotic, hybrid, or biological.

### ■ SIZE

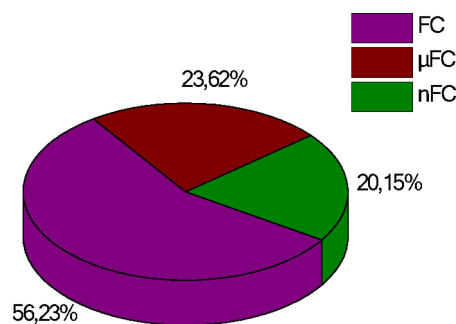
The dimensions of the channels for fluid delivery are an important feature to consider in the design of a fuel cell, especially with respect to the final application of the device. Different cell sizes can be found in the literature; the most important are fuel cells, microfluidic fuel cells,<sup>6</sup> and nanofluidic fuel cells (nFCs) (Figure 2).<sup>7</sup>

Figure 3 shows the publications from 2002 to 2022 ranking fuel cells by channel dimensions for fluid delivery, with 56% of the publications at FC. These types of FCs were first used mainly for hydrogen, alkali, direct methanol, and ethanol. With the advances of micromachining technologies and their commercialization, microfluidic devices have been developed with important advances, accounting for 24% of publications, while nFC are reported less with 20%, since equipment with higher precision is required to achieve nanometric channel dimensions.

The channel dimensions for FCs are particularly important for fuel cell design because in a micro- or nanodesign, the amount of fuel used is proportional to the energy produced compared to FCs, but the cost increases and the selectivity of



**Figure 2.** Schematic representation of the division of the FC according to the channel dimensions or the flow through the pores.



**Figure 3.** Representative graph of publications on fuel cells published between 2002 and 2022, sorted by size.

the fuel is not as specific. The channel size of the FC is determined by the final application of the device.<sup>4</sup>

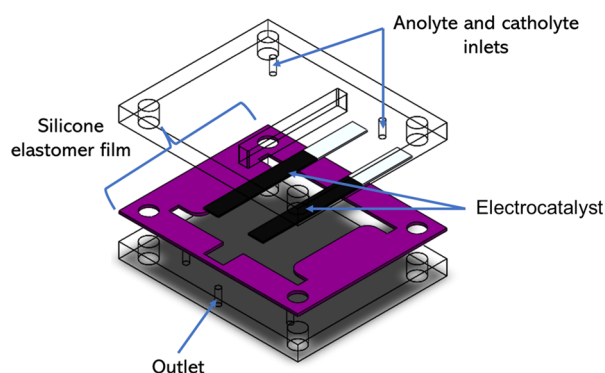
### ■ FABRICATION OF MICROFLUIDIC FUEL CELLS

The aim of this work is to provide a comparison of the state of the art specifically for  $\mu\text{FC}$ s in terms of electrocatalytic materials by type.

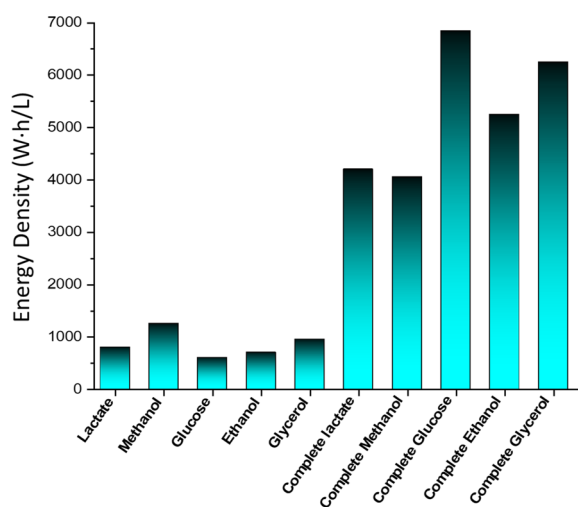
Although the fabrication processes of  $\mu\text{FC}$  can vary by author, the devices developed have typically used fabrication methods well known in electronics and microfluidic chips, such as photolithography.<sup>8–10</sup> Microchannels were cast in poly-(dimethylsiloxane) (PDMS) and sealed to a substrate that accommodated the electrode pattern. However, techniques such as 3D printing have opened up a new range of possibilities for custom development, particularly, the fused deposition modeling (FDM) technique, in which the model of the microfluidic fuel cell is designed using computer software that allows different channel configurations in one device (Figure 4).

### ■ FUEL

Each fuel has a different energy density depending on whether it is partially or fully oxidized. Conventionally, enzymes only oxidize the molecule to its next product, producing 1–4 electrons. For example, the oxidation of glucose to gluconic acid generates approximately 600 Wh/L, while complete oxidation could generate nearly 7000 Wh/L, which could be achieved with an enzyme cascade.<sup>11</sup> With abiotic catalysts, complete oxidation of the fuel can be achieved depending on the reaction mechanism, with higher power densities achieved in the complete oxidation of glucose, ethanol, and glycerol (Figure 5).

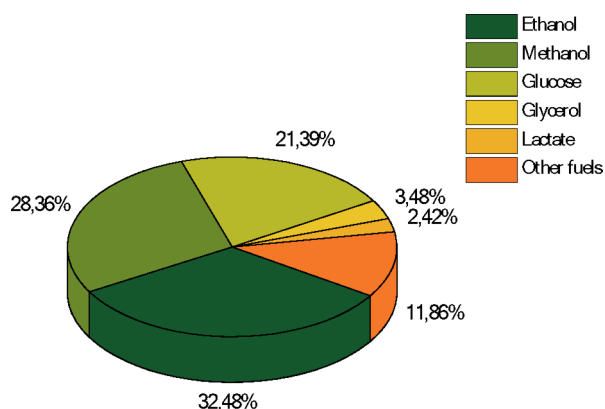


**Figure 4.** Schematic representation of a microfluidic fuel cell sandwich arrangement with two carbon electrodes and an air-breathing cathodic compartment.



**Figure 5.** Energy densities during partial and complete oxidation of fuel.

In the last 20 years (2002–2022), approximately 1 650 000 articles have been published on fuel cells considering the different types of fuels, which are shown in Figure 6. Approximately 32% (~536 000) of the reported fuel cells use ethanol as fuel, as this is the most frequently reported fuel for this type of technology, while lactate is the least frequently reported at about 2.4% (~39 900). In addition, fuel cell



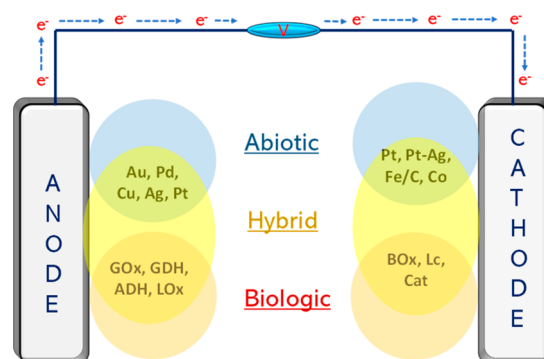
**Figure 6.** Representation of the percentage of published articles on fuel cells categorized by fuel type.

publications using other fuels, such as hydrogen, formic acid, vanadium, and urea, account for approximately 12% (~195 700).

It is evident that alcohols of different chains are the most common fuels because of their availability and versatility in catalysts. In this sense, lactate,<sup>12</sup> glucose,<sup>13</sup> and ethanol<sup>14</sup> are substances excreted by the human body, and approximately 56% of the reported fuel cells have the potential to work with human biofluids.

## ■ ELECTROCATALYTIC MATERIALS

In general, electrocatalytic materials for fuel oxidation or oxygen reduction can be divided into three different types: abiotic, hybrid, and biological (Figure 7). Abiotic electro-



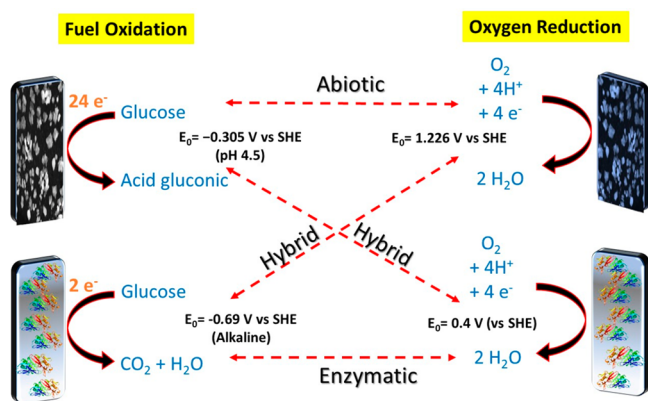
**Figure 7.** Scheme of a  $\mu$ FC classified by its catalysts.

catalysts usually use inorganic materials such as metals,<sup>15</sup> e.g., Au/Pani, Ni phosphate, or based on nanoporous multi-components.<sup>16,17</sup> The use of abiotic catalysts has advantages, such as a complete fuel oxidation with a greater generation of electrons and therefore output current, a higher catalytic rate, and a higher percentage of fuel utilization (FU). The main disadvantages are their limited activity and selectivity as well as deactivation in certain conditions such as pH, byproducts, and others.<sup>18</sup>

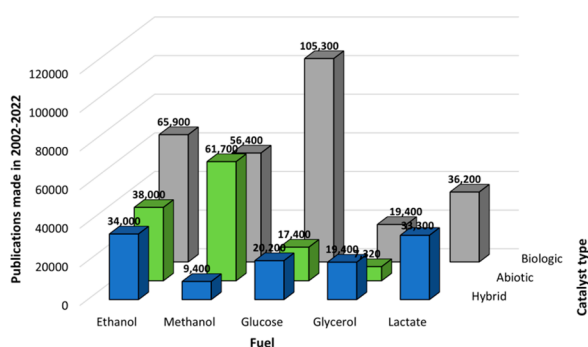
Biological electrocatalytic surfaces are based on living organisms, enzymes,<sup>19</sup> or microorganisms<sup>20</sup> that promote high selectivity in fuel oxidation. These biocatalysts are active at neutral or near-neutral pH and room temperature. Currently, there is continuous research on new modifications of enzymes, their isolation, and production or new applications such as the use of biofluids as blood, serum, tears, or sweat,<sup>21</sup> wastewater for energy production,<sup>22</sup> or implantable devices.<sup>23</sup> The disadvantage of using biocatalysts is their inactivation, limited lifetime, in some cases low reaction rate, low current, and output voltage.

Hybrid fuel cells (HFCs) are devices that integrate an abiotic and a biological catalyst in either the cathode or the anode to improve the electrocatalytic properties and power generation. In this way, the advantages of both catalyst types can be combined, such as higher voltage, current, and power density and selectivity, but also the disadvantages of each catalyst can be too (Figure 8).<sup>24,25</sup>

Figure 9 shows a classification according to the fuel and type of electrocatalyst with the proposed classification. Using a 3-axis diagram, it can be seen that glycerol has a higher work rate in a FC using abiotic materials compared to the biological catalyst, while for the other fuels, a greater number of devices use biological electrocatalytic materials than abiotic materials.



**Figure 8.** Illustration of glucose oxidation and enzymatic and abiotic oxygen reduction, showing the potentials and production of electrons and the importance of their combination with hybrid electrodes.



**Figure 9.** Publications on microfluidic fuel cells classified by fuel and type of electrocatalyst.

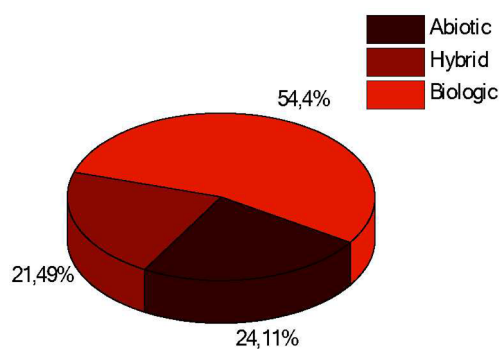
It can also be seen in Figure 9 that for glucose, more studies have been developed and published using abiotic and enzymatic electrocatalytic materials than on hybrid electrodes. On the other hand, for the oxidation of lactate, mainly hybrid and biological electrocatalysts have been reported, which have versatile applications for biofuels such as sweat or blood.<sup>26</sup>

The use of biofuels in  $\mu$ FCs has increased in publications every year, with glucose having the most publications even in the years of the COVID-19 pandemic (2020–2022).

It is worth noting that other published reviews have focused on FC theory, design classification, type of fuel, materials used, and nanomaterials, among others. It was found that only approximately 32% ( $\sim 520\,620$ ) of the publications classified the electrocatalysts used in fuel cells. Thus, this review covers the importance of  $\mu$ FCs and the different types of catalysts, including abiotic, biological, and hybrid, used for the oxidation of different fuels.

From this information, it can be concluded that modifications have probably been made to the electrocatalysts, but their classification was not considered to facilitate the search for this work.

Figure 10 shows the percentages of reported fuel cells that classified their electrocatalytic materials. It was found that 54% ( $\sim 283\,200$ ) of the above papers presented biological materials as electrocatalytic surfaces, which was found using keywords such as biological, enzymatic, and microbial. It was also found that abiotic materials still predominate over hybrid materials, which could be due to the novelty of the applications of hybrid catalytic materials in these technologies.



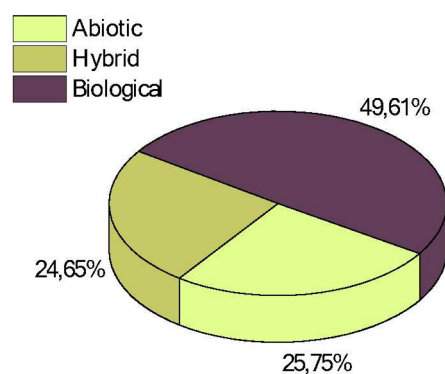
**Figure 10.** Percentage of publications (2002–2022) on fuel cells with electrocatalytic materials, categorized.

### ■ MICROFLUIDIC FUEL CELLS WITH DIFFERENT TYPES OF ELECTROCATALYTIC ELECTRODES

Specific information was collected focusing on the classification of electrocatalysts used in  $\mu$ FCs. The  $\mu$ FCs presented in this section are sorted by fuel and by the type of electrocatalytic materials through further processing of the collected information.

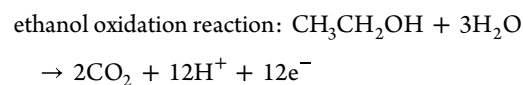
#### Ethanol

Ethanol has become an attractive fuel for  $\mu$ FC development due to its higher energy production, higher energy density ( $8.6\text{ kWh kg}^{-1}$ ), and environmental friendliness.<sup>27</sup> In Figure 11, the



**Figure 11.** Representative schematic of publications (2002–2022) on  $\mu$ FCs powered by ethanol, categorized by type of catalyst.

collected information is presented in a diagram where the  $\mu$ FCs using ethanol are classified according to the type of electrocatalytic electrode.



In this figure showing publications classifying electrocatalytic materials, biological catalysts dominate with 49% of the total, ahead of abiotic and hybrid materials. It can be concluded that hybrid materials have an advantage over abiotic materials in ethanol  $\mu$ FCs, although the number of publications is small ( $\sim 0.75\%$ ).

Several research works were consulted and considered to create comparative tables with the collected information on reported  $\mu$ FCs. This information is presented in Table 1, which compares different parameters. From Table 1, it can be seen that for the devices using ethanol as fuel, there is a

Table 1. Comparison of Ethanol Microfluidic Fuel Cells<sup>44</sup>

anode	cathode	catalyst	anolyte	AFR	catholyte	CFR	OCP (V)	$J_{\max}$ (mA cm <sup>-2</sup> )	$W_{\max}$ (mW cm <sup>-2</sup> )	ref
PtSn/C (70:30–20 wt %) hybrid 6.5 wt % SiO <sub>2</sub>	Pt/C (20 wt %, BASF)	abiotic	2.0 mol L <sup>-1</sup> EtOH	2 mL min <sup>-1</sup>	2.0 mol L <sup>-1</sup> EtOH	2 mL min <sup>-1</sup>	0.7	260.0	40.0	32
PtRu on carbon cloth	Ag–Pt (PLD)	abiotic	2 M EtOH in KOH	10 mL h <sup>-1</sup>	0.5 M KOH	10 mL h <sup>-1</sup>	0.8	54.0	10.0	28
NiO-YSZ	cathode powder/ethyl cellulose	abiotic	10%, 20%, and 30% EtOH/N <sub>2</sub>		ambient air		1.0	500.0	632.7	30
Pd/C AA	Pt/C AA	abiotic	2.0 mol L <sup>-1</sup> EtOH in KOH 1 mol L <sup>-1</sup>	1 mL min <sup>-1</sup>	oxygen humidified	200 mL min <sup>-1</sup>	0.9	65.0	18.0	33
np-ALCuNiPrPdCo	Pd <sub>3</sub> Pt <sub>3</sub> /Vn (Pd <sub>3</sub> Pt <sub>3</sub> ) <sub>10</sub> (CeO <sub>2</sub> NR) <sub>20</sub> (Vn) <sub>70</sub> Co@N–C from MOF	abiotic	0.5 M EtOH in 1.0 M KOH		oxygen		0.7	0.1	9.2	17
PdAg/MWCNT	Pd(Pd/C)	abiotic	3 M EtOH in 1 M KOH	12 mL h <sup>-1</sup>	1 M KOH/air breathing	12 mL h <sup>-1</sup>	0.2	26.0	4.4	34
NaNbO <sub>3</sub> –Pd/C	Pt/C AA	abiotic	1.0 mol L <sup>-1</sup> EtOH in KOH	1.0 mL min <sup>-1</sup>	oxygen	200 mL min <sup>-1</sup>	1.0	65.0	18.0	35
NaNbO <sub>3</sub> @Pd/C	Pt/C	abiotic	3 M EtOH in 3 M KOH	2 mL min <sup>-1</sup>	oxygen	100 mL min <sup>-1</sup>	0.7	120.0	15.0	36
Pd/Ni foam with HCl	Pd/NRGO	Abiotic	4 M EtOH in 2 M KOH		ambient air		0.8	200.0	31.5	37
Pd/Ni foam with mixed acids	Fe-NC/SN-CNT	abiotic	2 M EtOH in 2 M KOH	filled (12.5 mL)	ambient air		0.9	120.0	20.0	38
Pt/C	PDDA/Lac/HOOC-MWCNTs/PMG/Gr	biologic	1 mM EtOH-NAD <sup>+</sup> /O <sub>2</sub>	filled (10 mL)			0.5	0.2	4.0	39
PDDA/ADH/HOOC-MWCNTs/PMG/GC	Pt/C on Nafion	biologic	0.1 mol L <sup>-1</sup> EtOH in 10 mL of PBS pH 8.9	0.6 mL min <sup>-1</sup>	ambient air		0.5	2.1	0.3	40
poly(MG-PYR)ADH/MWCNT's	Pt on Nafion	biologic	100 mmol L <sup>-1</sup> EtOH and NAD 1.9 mmol L <sup>-1</sup>	filled (10 mL)	ambient air		0.7	0.8	0.3	41
ADH-PAMAM on carbon cloth	laccase-ABTS	biologic	160 μL of EtOH in 0.1 M PBS pH 9	16 μL min <sup>-1</sup>	0.1 M PBS pH 5	16 μL min <sup>-1</sup>	0.6	1.0	0.1	42
ADH	ELAT/E-TEK on Nafion	hybrid	100 mmol L <sup>-1</sup> EtOH PBS pH 7.2	filled (10 mL)	ambient air		0.6	1.0	0.2	43
ADH/MWCNT-Au	Pt/C	hybrid	1 mM EtOH/O <sub>2</sub> in PBS 1 mM NAD				0.3	16.0	1.7	14

<sup>a</sup>AFR: Anolyte flow rate. CFR: Catholyte flow rate. OCP: Open-circuit potential.  $J_{\max}$ : Maximum current density.  $W_{\max}$ : Power density.

tendency to avoid the use of catholytes and to perform the electrochemical reaction with an air-breathing cathode. This phenomenon can be explained by a simplification of the electrochemical reaction in  $\mu$ FCs to facilitate the operation with only one solution.<sup>28</sup>

It is also found that the open-circuit potentials (OCPs) range from 0.3 to 1.1 V depending on the catalyst used. From the information obtained, it can also be concluded that abiotic electrocatalytic materials tend to produce more energy in the fuel cell due to increased oxidation of the fuel, but biological materials maximize fuel selectivity, thus preventing catalyst poisoning and CO<sub>2</sub> generation. In addition, other reaction conditions can be used with biological catalysts, such as a neutral or slightly acidic pH, since, as shown in Table 1, laccases are used in the biocathode, which have their highest activity at a pH below 5.6 at a potential of 0.6 V, as reported by different authors.

For this reason, hybrid materials are becoming an interesting choice for electrocatalytic surfaces, as these materials utilize the properties of both biological and abiotic materials. Palladium (abiotic) and alcohol dehydrogenase (biological) are the most frequently cited reagents in the literature as electrocatalysts in ethanol  $\mu$ FCs. Ethanol is mostly used in solution with KOH at various concentrations, with the greatest potential coming from the cathode, since the oxidation process is thermodynamically 0.09 V (vs SHE).

Materials such as palladium, platinum, and their bimetallic mixtures (Pt–Ru) are used as abiotic electrocatalysts in most alkaline conditions: this is probably due to the conductive and catalytic properties of these materials, although there are many reports of work dealing with these materials.<sup>29</sup>

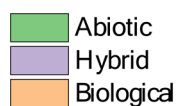
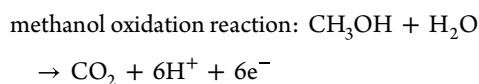
It has been observed that the density currents generated by abiotic materials are generally higher than those obtained by biological materials, which could be due to the phenomenon explained earlier that the fuel used with abiotic electrocatalysts is used in higher concentrations with a larger electrocatalytic surface area and a higher reaction rate compared to a biological fuel.

In this context, the authors have reported that the enzyme's response is promising for other applications in  $\mu$ FCs, for example, as a sensor in self-powered biofuel cells that use ethanol as fuel. Although there are more biological articles, modified metals have been shown to behave better under conditions similar to the end use of the device.

Yang, Liu, and co-workers,<sup>30</sup> presented a  $\mu$ FC with a higher current and power density of 500 mA cm<sup>-2</sup> and 632 mW cm<sup>-2</sup>, respectively, using an abiotic catalyst; however, ethanol is mainly intended as a fuel in industrial manufacturing and automotive applications processes.<sup>31</sup>

### Methanol

The use of methanol as a fuel in FCs is extremely attractive because the material is easy to obtain, transport, and store. In addition, the maximum voltage in FCs is comparable to that of another widely used fuel dihydrogen/dioxygen.<sup>44</sup> As seen in Figure 12, abiotic electrocatalytic materials account for most of the publications (49%), followed by biological electrocatalysts (43%), and finally hybrids (7.7%).



**Figure 12.** Publications between 2002 and 2022 on methanol microfluidic fuel cells ordered by type of electrocatalytic surface.

Table 2 shows similar behavior to ethanol fuel cells where the predominant catholyte is oxygen or ambient air. Metallic materials are mainly used to build the electrode, especially platinum,<sup>45</sup> but carbon-based materials such as graphite or Toray paper<sup>46</sup> are also commonly used as supports for the electrodes. Abiotic materials tend to produce a higher current density of 600 mA cm<sup>-2</sup> (80 °C) and a minimum of 0.5 mA cm<sup>-2</sup> when methanol is used at various concentrations ranging from 1 to 5 M.<sup>47</sup>

Another phenomenon to be observed is that the use of a flux decreases due to the  $\mu$ FC of the electrodes, and instead, a fixed volume of the sample contained in the device becomes more important, as in the reports of Cardoso and Neto,<sup>48,49</sup> where the volume of the sample was determined by a specific anode or cathode area; an important point to consider is the chemical reaction properties that take place in the area of interest.

In the case of methanol, the theoretical  $E_p$  is 1.21 V. The OCP presented in Table 2 shows voltages between 0.3 and 0.8 V, which is preferred when using the bimetallic material Pt–Ru and concentrations higher than 1 M methanol. Another parameter shown in Table 2 is that some works show a higher maximum current density, such as in ref 34, but neither a higher power density nor a higher OCP, which is interesting due to the impact of this behavior on the energy conversion of the device; in contrast, biological devices show a lower maximum current density, but the power density and OCP present the best quantity ratio in the whole device, as explained by Palmore et al.<sup>50</sup>

Methanol and ethanol are fuels with calorific value. Therefore, it can be observed that ethanol mixtures with other compounds favor the reaction by increasing the current and power values in the device, even more than the variations in the electrocatalysts used.

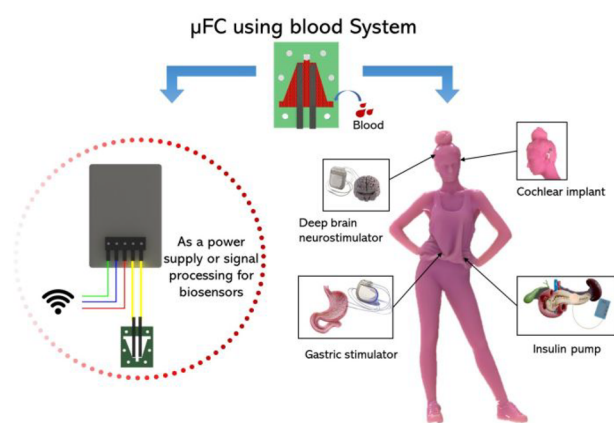
### Glucose

Glucose has advantages when used as a fuel in these technologies, primarily because it is found in living organisms that can be used as an energy source, creating an ideal environment for producing functional devices in vivo. Of the  $\mu$ FC systems that use glucose, others have been developed in which they are coupled with electronic devices such as self-powered sensors or implantable devices to harvest energy or glucose quantification (Figure 13). However, this fuel has limitations such as lower reaction kinetics and low efficiency.<sup>61</sup> The goal in designing this type of  $\mu$ FC is to develop an efficient electrocatalytic electrode in terms of durability and

Table 2. Comparison of Methanol Microfluidic Fuel Cells<sup>44</sup>

anode	cathode	catalyst	anolyte	AFR	catholyte	CFR	OCV (V)	$J_{\max}$ (mA cm <sup>-2</sup> )	$W_{\max}$ (mW cm <sup>-2</sup> )	ref
Nafion MEM, Pt/Ru	Pt/C	abiotic	1 mol L <sup>-1</sup> MOH/water + CH <sub>3</sub> OH	4 mL min <sup>-1</sup>	oxygen	200 mL min <sup>-1</sup>	0.3	30.0	6.3	51
TiCN-coated 316 L stainless steel	TiCN NCC	abiotic	0.05 M H <sub>2</sub> SO <sub>4</sub> + 2 ppm of HF + 20 mol L <sup>-1</sup> MOH	filled		filled	0.2	2600.0		47
Pt-Ru/C	Pt/C	abiotic	2 M aqueous MOH	2 mL min <sup>-1</sup>	oxygen	300 mL min <sup>-1</sup>	0.8	600.0	147.0	45
Ti	316 L, stainless steel	abiotic	7 M MOH + 3 mg/cm <sup>2</sup> Pt/Ru		hydrogen + air		0.2	12.0	5.2	52
4 mg/cm <sup>2</sup> Pt/Ru	0.5 mg/cm <sup>2</sup> Pt	abiotic	0.5 M MOH	10 mL min <sup>-1</sup>	air	600 mL min <sup>-1</sup>	0.3	190.0	40.0	53
SCITF nanosheets	Pt/Pt	abiotic	0.4 M MOH + Pt-Ru black		carbon-supported Pt-Pt		0.3	40.0	33.3	54
Pt-Ru/C (Vi-POSS-SO <sub>3</sub> Na)	Pt/C	abiotic	2 M MOH	500 sccm	oxygen	1 sccm	0.5	250.0	34.9	55
PS (Pt/G-CNT)	TSV	abiotic	2 M MOH	3 μL min <sup>-1</sup>	oxygen	inflow	0.5	5.0	0.3	55
PANI-A-BN/SPEEK-2	Pt black	abiotic	1 M MOH	5 mL min <sup>-1</sup>			0.2	130.0	11.4	56
Pt on carbon	Pt on carbon	abiotic	1 M MOH	5 mL min <sup>-1</sup>	oxygen	100 mL min <sup>-1</sup>	0.1	120.0	8.7	57
PTFE in toray	PTFE in sigracet	abiotic	4 M MOH	filled	water	filled	0.8	200.0	450.0	46
gCN	carbon	abiotic	0.5 M MOH in 0.5 M KOH				0.1	0.1		26
ZnO-gCN							0.1	0.2		
PdNPs-gCN							0.1	0.8		
PdNPs-ZnO-gCN							0.1	1.0		
1 mg/cm <sup>2</sup> Pt/Ru	Fe-N-C	abiotic	5 M MOH	5 mL min <sup>-1</sup>	oxygen	100 mL min <sup>-1</sup>	0.5	75.0	54.0	58
AOx	laccase	biologic	1 M MOH in KPBS (0.1 M pH 7.5)	0.2 mL min <sup>-1</sup>	oxygen/air	0.7 L min <sup>-1</sup>	0.6	0.3	46.0	59
CC-NP-AOx-CS	CC-NP-BOx-CS	biologic	1 M MOH	filled (10 mL)			0.7	0.1	0.0	60
ELAT in Nafion/PtRu	PP-ABTS-LAC	biologic	100 mmol L <sup>-1</sup> MOH in acetate buffer pH 4.5	filled (10 mL)			0.4	0.1	25.4	48
ELAT in Nafion	PyS laccase (purified)	biologic	100 mmol L <sup>-1</sup> MOH in 50 mol L <sup>-1</sup> PBS pH 5.0	filled (10 mL)			0.3	0.9	0.1	49
	PyS laccase (crude)						0.3	0.6	0.1	
graphite plate	Pt gaze	biologic	0.1 M CH <sub>3</sub> OH + 5 U FDH + 40 U AldDH + 11 U ADH + 1 .0 mM NAD <sup>+</sup> + 50 mM BV2 + 1.7 U diaphorase + 1 M LiCl in 0.1 M Tris buffer, pH 7.5	75 mL	1 M LiCl, 0.1 M Tris buffer, pH 7.5/O <sub>2</sub>	50 mL	0.8	2.5	0.7	50

<sup>a</sup> AFR: Anolyte flow rate. CFR: Catholyte flow rate. OCP: Open-circuit potential.  $J_{\max}$ : Maximum current density.  $W_{\max}$ : Power density.



**Figure 13.** Application of  $\mu$ FCs with coupling to electronic or implantable devices.

reduction of charge on the noble metal to increase the fuel cell performance.<sup>62</sup>

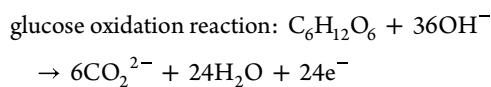
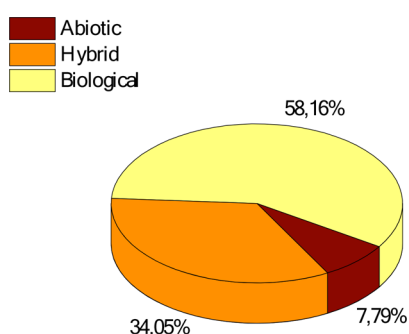


Figure 14 shows the percentages obtained with glucose microfuel cells, ordered by the type of electrocatalytic material.



**Figure 14.** Publications between 2002 and 2022 on glucose microfluidic fuel cells, ordered by electrocatalyst type.

In this case, most of the reported electrocatalysts are biological (58%), followed by hybrid materials (34%). Based on the use of a biofuel with enzyme or microbial electrocatalysts, the appropriate fuel source can be selected. A total of 7.8% of the hybrid electrodes is better than the abiotic materials, which is an important factor to be considered due to the novel application of synthesized abiotic and biological materials to produce new hybrid materials as electrocatalytic materials to improve the energy generated in the  $\mu$ FC.

In this case, it was found that most of the reported electrocatalytic materials are enzymes such as glucose oxidase (GOx) or glucose dehydrogenase (GDH) because they are versatile, inexpensive, easily accessible, and catalytically active. It was also found that hybrid electrocatalytic materials (34%) have an advantage over abiotic materials (7.8%); this is a key factor due to the intrinsic properties of the catalysts using the combination of electrocatalytic and reaction conditions.

Table 3 shows the collected data from several  $\mu$ FCs using glucose as fuel. In  $\mu$ FCs, Au/C and its mixtures, such as AuAg/C and Au/ZnO, on various carbon nanomaterials are used for glucose oxidation at the anode, while Pt is widely used for

oxygen reduction at the cathode. C and PtAg/C is used because it is reportedly more selective and reduces poisoning. The reaction conditions for the oxidation of glucose in  $\mu$ FC are generally alkaline with limited response in the oxygen reduction reaction due to its low saturation in aqueous solution. For this reason, air-breathing devices that take ambient oxygen have been implemented in the designs. The main advantage of these abiotic catalysts is that they can fully oxidize glucose using  $24\text{e}^-$  and have a lower theoretical oxidation potential of  $-0.69\text{ V}$  (vs SHE), which could reach the theoretical potential of  $1.78\text{ V}$  (vs SHE) and even a higher voltage if the RRO is also under optimal conditions. Table 3 also shows maximum OCPs of  $0.8\text{ V}$  by Arjona et al.<sup>63</sup> and Cuevas-Muñiz et al.<sup>64</sup> using  $10$  and  $100\text{ mM}$  glucose in KOH, respectively. The highest reported current densities are  $75\text{ mA cm}^{-2}$  (shown in the polarization graph) by U S and Goel<sup>68</sup> and  $9.5\text{ mA cm}^{-2}$  by Arjona et al.,<sup>63</sup> while the maximum power densities are  $620$  and  $500\text{ }\mu\text{W cm}^{-2}$  by Cuevas-Muñiz et al.<sup>64</sup>

On the other hand, the use of GOx and GDH in the anode and laccase (Lc) and bilirubin oxidase (BOx) in the cathode has been reported preferentially in microfluidic biofuel cells. The latter is due to their high potential in the ORR of  $0.6\text{ V}$  (vs Ag/AgCl), their operation at slightly acidic pH between  $4.5$  and  $5.6$  for Lc and neutral pH values for BOx, which could be advantageous in applications involving human fluids such as blood, sweat, tears, and saliva.

Table 3 shows that for  $\mu$ FCs with enzymes, some OCPs are similar to the abiotic ones and higher ( $1.3\text{ V}$ ) when a stack connected in series is used. The highest current and power densities are  $2\text{ }\mu\text{A cm}^{-2}$  and  $580\text{ }\mu\text{W cm}^{-2}$ , respectively, as reported by Escalona-Villalpando et al. when four cells are in series, parallel, and series/parallel. The performance with H $\mu$ FC is comparable to enzymatic and abiotic  $\mu$ FCs with higher power densities than biological  $\mu$ FCs.

In general, the reported devices using GLU as fuel require a remarkably small amount of fuel, almost as small as the amount of GLU in sweat.<sup>65</sup> As mentioned earlier, the use of glucose as fuel offers the possibility of using biofluids, such as sweat, as fuel. Work such as that of Escalona-Villalpando et al. has shown higher power density using a hybrid material with one of the lowest anolyte flow rates.<sup>66</sup>

### Glycerol

In the case of glycerol as a fuel,  $\mu$ FC has been found to be inexpensive and easy to store and has a higher theoretical energy density ( $6.4\text{ kWh L}^{-1}$ ).<sup>80</sup> In addition, glycerol has high fuel efficiency and is a product derived from biodiesel triglycerides.<sup>16</sup>

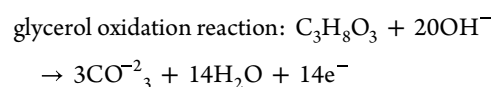


Table 4 shows different  $\mu$ FCs that use glycerol. It also shows that palladium (Pd), platinum (Pt), and binary metals (Cu, Fe) are widely used mainly because of their catalytic properties on hydroxyl groups in alkaline medium or neutral buffer. The highest OCP ( $1.7\text{ V}$ ) was reported,<sup>81</sup> which was achieved by optimizing the reaction conditions of the anode and cathode, catalyst amount, and temperature. Similarly, Sangkheaw et al. reported a maximum current and power density of  $502\text{ mA cm}^{-2}$  and  $330\text{ mW cm}^{-2}$ , respectively. The biological catalysts reported for glycerol oxidation were the enzymes pyrroloquinoline quinone-dependent alcohol dehydrogenase (PQQ-



Table 3. Comparison of Glucose Microfluidic Fuel Cells<sup>a</sup>

anode	cathode	catalyst	anolyte	AFR	catholyte	CFR	OCP (V)	$J_{\max}$ (mA cm <sup>-2</sup> )	$W_{\max}$ ( $\mu$ W cm <sup>-2</sup> )	ref
Au/MWNTCs	Pt/V XC-72 (30 wt %)	abiotic	10 mM D(+)-GLU in 0.3 M KOH	0.042 mL min <sup>-1</sup>	oxygen in 0.3 M KOH	0.110 mL min <sup>-1</sup>	0.7	1.2	280.0	67
AuAg/MWCNT	Pt/C (air exposed)	abiotic	10 mM D(+)-GLU in 0.3 M KOH	1.5 mL h <sup>-1</sup>	0.3 M KOH	2.5 mL h <sup>-1</sup>	0.8	9.5	160.0	63
gold solution	CuSO <sub>4</sub> and Na <sub>2</sub> SO <sub>4</sub>	abiotic	40 mM D(+)-GLU in 0.1 M PBS	capillarity	oxygen-saturated 0.1 M PBS	capillarity	0.4	75.0*	12.5	68
Au/Pani	Pt/V XC-72 (30 wt %)	abiotic	10 mM D(+)-GLU in 0.3 M KOH	0.042 mL min <sup>-1</sup>	oxygen in 0.3 M KOH	0.110 mL min <sup>-1</sup>	0.5	0.6	180.0	69
Au/C	Pt/V XC-72 (30 wt %)	abiotic	10 mM D(+)-GLU in 0.3 M KOH	0.042 mL min <sup>-1</sup>	oxygen	0.110 mL min <sup>-1</sup>	0.3	1.5	500.0	64
ZnO/Au 3%	Pt/C (exposure to air)	abiotic	4.65 mM D(+)-GLU in human blood	0.5 mL h <sup>-1</sup>	air breathing		0.7	0.8	330.0	70
AuAg/C	PtAg/C	abiotic	100 mM D(+)-GLU in KOH	100 $\mu$ L min <sup>-1</sup>	oxygen in 0.3 M KOH	500 $\mu$ L min <sup>-1</sup>	0.8	2.2	620.0	64
CB-MWCNT/GOx/Nafion	CB-PBSE-BOX	biologic	10 mM D(+)-GLU in 0.1 M PBS (pH 7.0)	finger powered	0.1 M PBS, pH 7.0, air saturated	finger powered	0.4	0.6	28.0	71
RGO/AuNPs/PNR/GOx	RGO/AuNPs/PNR/LAC	biologic	180 mM D(+)-GLU in physiological serum (pH 5.5)	50 $\mu$ L min <sup>-1</sup>	physiological serum (pH 5.5)	50 $\mu$ L min <sup>-1</sup>	0.2	0.1	3.6	72
GOx/MWCNT	laccase/MWCNT	biologic	100 mM D(+)-GLU	400 $\mu$ L min <sup>-1</sup>	oxygen ABTS	400 $\mu$ L min <sup>-1</sup>	0.4	0.1	18.0	73
Au	Au	biologic	0.5 mg mL <sup>-1</sup> GOD/10 mM Fe(CN) <sub>6</sub> <sup>3-</sup> in 0.2 M phosphate buffer pH 7	1 mL min <sup>-1</sup>	0.5 mg mL <sup>-1</sup> LAC/5 mM ABTS in 0.2 M citrate buffer pH 3	1 mL min <sup>-1</sup>	0.6	0.7	110.0	74
GDH	BOX	biologic	30 mM D(+)-GLU		air breathing		0.7	0.3	20–90	75
<i>Aspergillus niger</i> GOx/MWCNT	laccase/MWCNT	biologic	100 mM D(+)-GLU in PBS pH 7.4	0.5 $\mu$ L min <sup>-1</sup>	0.5 mg mL <sup>-1</sup> LAC in PBS pH 4.5	0.5 $\mu$ L min <sup>-1</sup>	0.5	0.6	104.2	19
Ni-E. coli	carbon cloth	biologic	6.6 mM D(+)-GLU	1 mL h <sup>-1</sup>	PBS pH 5.6 (0.1 M)	3 mL h <sup>-1</sup>	0.5	386 A m <sup>-3</sup>	5.2	76
HQ-LPEI/GDH (on TC-PTFE)	AnMWCNT/BOX	biologic	100 mM D(+)-GLU in PBS pH 7.4	3 mL h <sup>-1</sup>			0.8	1.4	360.0	77
GOx/MWNTC's-GA	Pt/C	hybrid	5 mM D(+)-GLU in PBS (pH 7.0)	8.33 $\mu$ L min <sup>-1</sup>	air breathing		1.3	2.0	580.0	
maghemite NP/GOx	Pt NP	hybrid	100 mM D(+)-GLU	0.06 mL min <sup>-1</sup>	oxygen-saturated PBS	0.21 mL min <sup>-1</sup>	0.3	0.3	30.0	78
Ni-E. coli	carbon cloth	hybrid	1.1 mM D(+)-GLU	200 $\mu$ L h <sup>-1</sup>			1.8	14.9 A m <sup>-3</sup>	20 W m <sup>-3</sup>	79
							2.1	26.3 A m <sup>-3</sup>	38.2 mW m <sup>-3</sup>	

<sup>a</sup> AFR: Anolyte flow rate. CFR: Catholyte flow rate. OCP: Open-circuit potential.  $J_{\max}$ : Maximum current density.  $W_{\max}$ : Power density.

Table 4. Glycerol Microfluidic Fuel Cell Comparison<sup>a</sup>

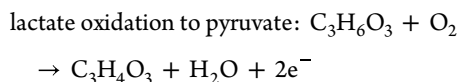
anode	cathode	catalyst	anolyte	AFR	catholyte	CFR	OCV (V)	$J_{\max}$ (mA cm <sup>-2</sup> )	$W_{\max}$ (mW cm <sup>-2</sup> )	ref
PdAg/CNT/PTFE	carbon paper (Fe-based catalyst)	abiotic	6.0 M KOH + 3 M glycerol	4 mL min <sup>-1</sup>	oxygen	200 mL min <sup>-1</sup>	0.9	43.4	214.7	84
MEA3 Pt/C	Pt/C	abiotic	1 M glycerol + 5 M NaOH	1 mL min <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub>	6 mL min <sup>-1</sup>	0.4	451.4	375.0	85
20% Pt/C	ELAT GD/L	abiotic	1 mol L <sup>-1</sup> glycerol + 4 mol L <sup>-1</sup> KOH	1 mL min <sup>-1</sup>	oxygen	30 mL min <sup>-1</sup>	0.5	15.1	20.0	86
60% Pt/C	ELAT GD/L	abiotic	1 mol L <sup>-1</sup> glycerol + 4 mol L <sup>-1</sup> KOH	1 mL min <sup>-1</sup>	oxygen	30 mL min <sup>-1</sup>	0.4	19.6	35.0	
Cu@Pd/C	Pt/C	abiotic	5 vol % glycerol + 0.3 M KOH	2 mL h <sup>-1</sup>	air + oxygen	4 mL h <sup>-1</sup>	0.7	97.6	17.4	87
Cu@Pt/C	Pt/C	abiotic	5 vol % glycerol + 0.3 M KOH	2 mL h <sup>-1</sup>	air + oxygen	4 mL h <sup>-1</sup>	0.8	104.1	23.2	
Pt <sub>1</sub> Au <sub>1</sub> /VGCNF with 15 wt % PTFE	Pt/C	abiotic	5 M NaOH + 2 M glycerol		air + oxygen		0.8	86.6	70.0	80
Pd black	Pt black	abiotic	1 M glycerol + 2 M NaOH	2 mL min <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> + 1 M H <sub>2</sub> SO <sub>4</sub>	5 mL min <sup>-1</sup>	0.9	100.0	275.0	88
Pd(DBA) <sub>2</sub>	Fe-Co hypermec K-14	abiotic	5 wt % glycerol + 10 wt % KOH		air		0.8	16.0	24.0	89
Au/C (PTFE)	Fe-Co-based 4020	abiotic	1 M glycerol + 8 M OH		oxygen	0.4 L min <sup>-1</sup>	1.0	200.0	43.9	90
Au/C + 10 wt % Teflon	Fe-Cu-N <sub>4</sub> /C	abiotic	2 M KOH + 1 M glycerol	4 mL min <sup>-1</sup>	oxygen	0.4 L min <sup>-1</sup>	0.7		57.9	91
Au/C + 10 wt % Teflon	Fe-Cu-N <sub>4</sub> /C	abiotic	2 M KOH + 1 M crude glycerol	4 mL min <sup>-1</sup>	oxygen	0.4 L min <sup>-1</sup>	0.7		30.7	
NiPt/Pt-Fe <sub>2</sub> O <sub>3</sub>	Pt wire	abiotic	0.1 mol L <sup>-1</sup> PBS + 0.1 mol L <sup>-1</sup> glycerol		0.1 mol L <sup>-1</sup> PBS + 0.1 mol L <sup>-1</sup> glycerol		0.5	1.0	0.1	16
Pt-Fe <sub>2</sub> O <sub>3</sub>	Pt wire	abiotic	0.1 mol L <sup>-1</sup> PBS + 0.1 mol L <sup>-1</sup> glycerol		0.1 mol L <sup>-1</sup> PBS + 0.1 mol L <sup>-1</sup> glycerol		0.4	0.6	0.0	
AA-DGFC with Pt/C	BL coated	abiotic	1.0 M glycerol + NaOH	1 mL min <sup>-1</sup>	1.0 M H <sub>2</sub> O <sub>2</sub> + 1 M H <sub>2</sub> SO <sub>4</sub>	4 mL min <sup>-1</sup>	1.7	501.7	330.0	81
Pt/C-modified CP (FeCl <sub>3</sub> /mM decorated)	Pt/C-modified CP	abiotic	N <sub>2</sub> -saturated 0.05 M glycerol in 1 M KOH	1 μL min <sup>-1</sup>	O <sub>2</sub> in 1 M H <sub>2</sub> SO <sub>4</sub>	1 μL min <sup>-1</sup>	1.2	87.6	39.4	92

<sup>a</sup>AFR: Anolyte flow rate. CFR: Catholyte flow rate. OCV: Open-circuit potential.  $J_{\max}$ : Maximum current density.  $W_{\max}$ : Power density.

ADH) together with PQQ-dependent aldehyde dehydrogenase (PQQ-AldDH), and after the reaction cascade with oxalate oxidase, in both cases, Pt/C was used as a cathode with excellent results, although not in a microfluidic system.<sup>82,83</sup>

### Lactate

Lactate, as an alternative fuel, has high energy densities of 507 and 3041 Wh/L under partial and complete oxidation, respectively, as shown in Figure 5, comparable to other fuels. Lactate is not one of the most widely reported fuels in FCs, but it has the distinction of being able to be used for bioenergy applications, i.e., the energy can be produced by components of living organisms, in this case from sweat, which has a concentration above 40 mM during physical activity.<sup>93</sup> Abiotic catalysts for lactate oxidation derived from NiO, amino-TEMPO, and CuO have been reported, but they have not been used in  $\mu$ FC.<sup>94–96</sup>



Here, the published articles indicated the type of electrocatalytic materials used in the device, whether enzymatic, microbial, nonenzymatic, abiotic, or hybrid.

Figure 15 shows that most of the reported  $\mu$ FCs (53%) used biological electrocatalytic electrodes, as in the case of glucose,

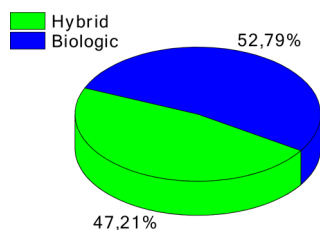


Figure 15. Publications between 2002 and 2022 on lactate microfluidic fuel cells, ordered by electrocatalytic material.

followed by hybrid electrocatalytic electrodes, which accounted for 47%, but no abiotic electrocatalytic materials were found compared to other fuels; this means that in lactate, the preference for biological materials, whether enzymes or microorganisms, is pronounced, and it can be observed that hybrid materials have been used in several studies when they can improve the performance of the electrocatalytic properties instead of trying abiotic materials.

As with all  $\mu$ FCs, the design is based on the expected application of the device, which includes the materials to be used as well as the channels and size of the fuel cell.

Table 5 shows some of those  $\mu$ FCs found in this study.

For hybrid and biological  $\mu$ FCs, the use of lactate oxidase (LOx) or lactate dehydrogenase (LDH) has been reported preferentially for lactate oxidation to pyruvate at slightly acidic or neutral pH values.<sup>97</sup> As electrocatalysts in hybrid  $\mu$ FCs, Pt/C and AgO were reported for the cathode and Lc and Box for the biological.<sup>98</sup>

Several of the reported hybrid and biological  $\mu$ FCs using lactate as fuel have been evaluated in a single-chamber fuel cell (SC), but the implementation of the microfluidic system improves the overall performance. We have previously reported that using a microfluidic device with an independent inlet for the anolyte/catholyte could increase OCP by using

the optimal pH of each enzyme and increasing current and power densities.

The use of carbon-based materials and nanostructured materials as supports or electrodes in fuel cells is also widespread. There are two specific cases that stand out from other works, namely, those of Sanchez et al. and Baniyadi et al.,<sup>22,99</sup> where the reported power density and maximum current density are markedly higher than those of the other works listed in Table 5.

The perspective of the presented works, when using lactate as fuel, as in glucose-powered devices, aims at in vivo devices using biological fluids. However, abiotic materials are not discussed in the reviewed literature, which is a notable difference in the authors' approach in developing these devices compared to other fuels with the same goal; therefore, enzyme-based electrocatalysts are the most developed since lactate is found in fluids with different interfering factors according to different authors and enzymes solve selectivity problems.

## SUMMARY AND PERSPECTIVES

In general, there is a clear trend in the development of electrocatalytic materials used in  $\mu$ FCs, especially where biological electrodes interact with abiotic materials to create hybrid interfaces that take advantage of the best properties of both systems.

Additionally, in this work, there are a variety of  $\mu$ FCs that generate energy using different fuels. Here, the fuels that have been discussed with the most importance are methanol, ethanol, glucose, lactate, and glycerol.

In the case of ethanol, the wide range of materials used is striking, especially those based on elements such as Pd or Pt for their catalytic properties. The maximum current densities range from 120 and 2020 mA cm<sup>-1</sup> with OCPs close to 1 V. One of the main difficulties in developing these devices is the cost, since the materials used are extremely expensive, and in addition, ethanol is used as fuel in the solutions of the devices presented, which reduces the current generation.

It is well known that methanol is one of the cheapest and easiest fuels to obtain. However, the use of structures based on precious metals such as palladium and other very rare metals such as ruthenium or transition metals such as nickel is expensive compared to others. One of the observed features is that the  $\mu$ FCs that have the best reliability are based on carbon structures with maximum current densities up to 2600 mA cm<sup>-1</sup> synthesized with the above-mentioned metals. One of the observed problems is that the reported OCP is generally less than 1 V.

On the other hand, the ability to use biofluids such as sweat for energy production has enabled the development of  $\mu$ FCs that use glucose as fuel. These cells have a density of up to 75 mA cm<sup>-1</sup> and an OCP of nearly 1 V, which is much lower than that of other fuels but still opens a great development opportunity for an energy alternative for daily life since energy can be efficiently extracted from sweat-like fluids. A variety of material combinations can be observed in this type of device, especially metallic combinations with enzymes such as GOx, which makes commercial use attractive.

For devices using glycerol as fuel, there is already a clear trend toward the use of abiotic materials, all of which are clearly classified, indicating a deeper exploration and development of materials. In general, much lower current densities are recorded, but this work reports good stability and lifetime with OCPs near 1 V. The trending material is carbon in multiple

Table 5. Comparison of Lactate Microfluidic Fuel Cells<sup>a</sup>

anode	cathode	catalyst	anolyte	AFR	catholyte	CFR	OCP (V)	$J_{\max}$ (mA cm <sup>-2</sup> )	$W_{\max}$ ( $\mu$ W cm <sup>-2</sup> )	ref
carbon cloth	carbon cloth	hybrid	<i>S. oneidensis</i> MRI	50 $\mu$ L h <sup>-1</sup>	50 mM K <sub>3</sub> Fe(CM) <sub>6</sub> in 100 mM PBS pH 7.0	50 $\mu$ L h <sup>-1</sup>	0.6	0.0	62.5 W m <sup>-3</sup>	20
LOx/1-methoxy PMS	BOx/ABTS modified	biologic	300 mM lactate in 1.5 M PBS		oxygen		0.5	0.7	4300.0	100
<i>A. butzleri</i> OK-1	potassium ferricyanide	biologic	5.5 mM lactate	8.33 $\mu$ L min <sup>-1</sup>						
LOx/FeMe <sub>2</sub> -LPEI	Lc/PyrAn-MWCNT	biologic	20 mM lactate in PBS pH 5.6, 10 mM Lac	3 mL h <sup>-1</sup>	0.2 M PBS pH 5.6	3 mL h <sup>-1</sup>	0.7	0.3	48.8	98
NAD dependent (LDH)	ELAT (GDE) 20 wt % Pt on carbon	biologic	100 mM lactate with 1 mM NAD <sup>+</sup> in PBS	1.5 mL h <sup>-1</sup>	air breathing			0.2	44.0	102
NAD dependent (LDH, PDH)	ELAT (GDE) 20 wt % Pt on carbon	biologic	100 mM lactate with 1 mM NAD <sup>+</sup> in PBS	1.5 mL h <sup>-1</sup>	air breathing			0.2	61.0	102
NAD dependent (LDH, PDH, CS, aconitase, IDH)	ELAT (GDE) 20 wt % Pt on carbon	biologic	100 mM lactate with 1 mM NAD <sup>+</sup> in PBS	1.5 mL h <sup>-1</sup>	air breathing			0.3	80.0	102
NAD dependent (LDH, PDH, CS, aconitase, IDH, KDH)	ELAT (GDE) 20 wt % Pt on carbon	biologic	100 mM lactate with 1 mM NAD <sup>+</sup> in PBS	1.5 mL h <sup>-1</sup>	air breathing			0.4	141.0	102
NAD dependent (LDH, PDH, CS, aconitase, IDH, KDH, succinyl CoA synthetase, SDH)	ELAT (GDE) 20 wt % Pt on carbon	biologic	100 mM lactate with 1 mM NAD <sup>+</sup> in PBS	1.5 mL h <sup>-1</sup>	air breathing			0.8	227.0	102
NAD dependent (LDH, PDH, CS, aconitase, IDH, KDH, succinyl CoA synthetase, SDH, fumarase, MDH)	ELAT (GDE) 20 wt % Pt on carbon	biologic	100 mM lactate with 1 mM NAD <sup>+</sup> in PBS	1.5 mL h <sup>-1</sup>	air breathing			3.3	827.0	102
electrospun carbon/ <i>S. oneidensis</i>	carbon felt	biologic	30 mM lactate/ <i>S. oneidensis</i> MRI		150 mM NaCl and 100 mM K <sub>3</sub> Fe(CM) <sub>6</sub>		0.8	140.0	56 000.0	22
MWCNT/NQ/LOx	Pt/C and hydrogel	biologic	15 mM lactate solution	0.042 mL min <sup>-1</sup>	air breathing		0.4	0.2	62.2	103
amino-TEMPO/OxDc	Pt	biologic	100 mM lactate	1 mL h <sup>-1</sup>	oxygen			23.0		95
SB4 enrichment	Pt	biologic	20 mM lactate	40 mL min <sup>-1</sup>	artificial sweat	40 mL min <sup>-1</sup>	0.8	0.0	8 W m <sup>-3</sup>	104
LOD-based fiber	BOD/CNT/PTFE-CNT/fiber	biologic	20 mM lactate in artificial sweat	0.5 mL h <sup>-1</sup>	artificial sweat		0.4	8.8	250.0	105
LOx-BSA solution (agarose gel) on carbon cloth	carbon cloth/PTFE (out) an Pt (inside)	biologic	80 mM lactate in simulated sweat	200 $\mu$ L h <sup>-1</sup>	simulated sweat		0.6		900.0	106
LOx/TCP	Lc/An-MWCNT	biologic	real sweat		real sweat		0.6	0.2	64.0	107
graphite round rod	graphite round rod	biologic	15 mM lactate/ <i>S. oneidensis</i> MRI/N <sub>2</sub>		ferricyanide (100 mM) in PBS 100 mM pH 7.0		0.5	366.0	144 000.0	99

<sup>a</sup>AFR: Anolyte flow rate. CFR: Catholyte flow rate. OCP: Open-circuit potential.  $J_{\max}$ : Maximum current density.  $W_{\max}$ : Power density.

structures with different metals, although its use in microfluidic fuel cells has lost influence, as glycerol requires more specific processes for extraction.

Finally, lactate, similar to glucose, is easily extracted from biofluids. Theoretical current densities of up to  $4300 \text{ mA cm}^{-1}$  with OCP values greater than 1 V could be achieved with these devices, which is a large energy production for a fuel that occurs in dilute form in various solutions. This large energy generation is due to the use of biological materials such as enzymes and microbes with carbon-based electrodes, which provide an ideal environment for the interaction between the enzymes/microbes and the fuel to take full advantage of the chemical reaction.

It can be observed that the progress in the development of  $\mu\text{FCs}$  is focused on the use of materials with a good efficiency–cost ratio without neglecting the sustainability of the energy obtained. Likewise, the trend is toward the use and development of hybrid catalysts to achieve the ratio targeted by different research groups, such as the group led by Arriaga, in which  $\mu\text{FCs}$  have been developed with different materials such as platinum–silver alloys,<sup>28</sup> nickel/iron nanoparticles,<sup>108</sup> or palladium/cobalt aerogels,<sup>109</sup> showing an improvement in electrocatalytic activity for application to different fuels.

Advances in  $\mu\text{FC}$  research have increased due to their versatility, simple design, miniaturization, and ease of use. In the power generation field, there is interest in  $\mu\text{FCs}$  because they can be used to miniaturize components, reduce costs, and use energy more efficiently, in addition to being able to use various alternative fuels such as glucose, alcohols, glycerol, and even waste. The versatility of catalysts is important because not only can abiotic catalysts be used but other catalysts, such as enzymes and microorganisms, are also very well suited for this type of microfluidic system. However, despite significant progress in the research and development of  $\mu\text{FCs}$ , there is still no practical application in which they can be used. Occasionally,  $\mu\text{FCs}$  depend on other devices that consume energy to function, such as pumps or valves. With advances in research and development, the barriers separating the opportunities and prospects for applying  $\mu\text{FCs}$  to devices with functional and real-world applications have been minimized.

### CONTRIBUTION OF THE RESEARCH GROUP TO MICROFLUIDIC FUEL CELLS WITH DIFFERENT FUELS

The National Micro- and Nanofluidic Laboratory research group has made a significant contribution to power generation using various alternative fuels, electrocatalysts, and several microfluidic devices. As shown in Figure 16, the most common fuel released by  $\mu\text{FCs}$  in research is glucose because it is abundant, economically accessible, of high energy density ( $4430 \text{ Wh kg}^{-1}$ ), and found in biological fluids such as blood and serum. Aliphatic alcohols such as ethanol, methanol, and glycerol were also commonly used and accounted for 35% of published articles. The least common fuel reported as a group is lactate, which plays an important role as an energy source in biological fluids.

The  $\mu\text{FC}$  of glucose is the most frequently published one using different electrocatalysts: 43% with abiotic materials such as Au, Au/MWCNT, Au/PANI, and AuAg/C; 33% hybrids mainly using glucose oxidase enzyme (GOx) or Au/C at the anode; while Pt/C or laccase (Lc) were frequently used at the cathode and 24% used enzymatic catalysts with GOx or

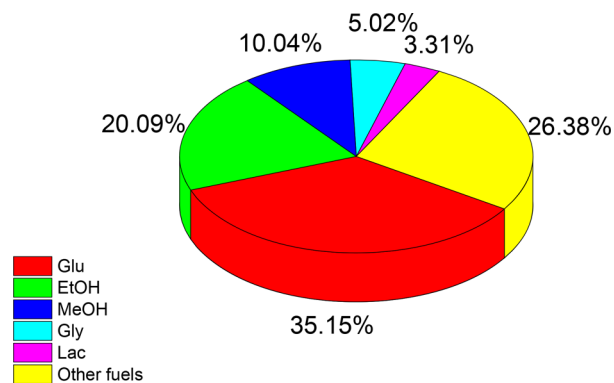


Figure 16. Alternative fuels reported by the working group in  $\mu\text{FCs}$ .

glucose dehydrogenase (GDH) enzyme at the bioanode and laccase or bilirubin oxidase (BOx) at the biocathode. While three times more abiotic catalysts were used in the ethanol  $\mu\text{FCs}$  than in the hybrids, catalysts for the ethanol oxidation reaction, such as PtAg, PtCu, Pd–NiO, Pd/C, and alcohol dehydrogenase (ADH), were used in the hybrid anode, while Pt/C was used in the cathode.

In contrast, only abiotic catalysts were used for methanol and glycerol, mostly Pd derivatives such as Pd aerogel, Pd nanocubes, PdCo, Pd/MWCNT, PdAg, PdMo/C, and Cu@Pd or other noble metals such as Pt, PtAg, Cu@Pt/C. Otherwise, only enzymatic catalysts such as lactate oxidase (LOx) and Box were used in the  $\mu\text{FC}$  with lactate.

The other fuels described in Figure 17 are those published by the research group and are not discussed in this work.

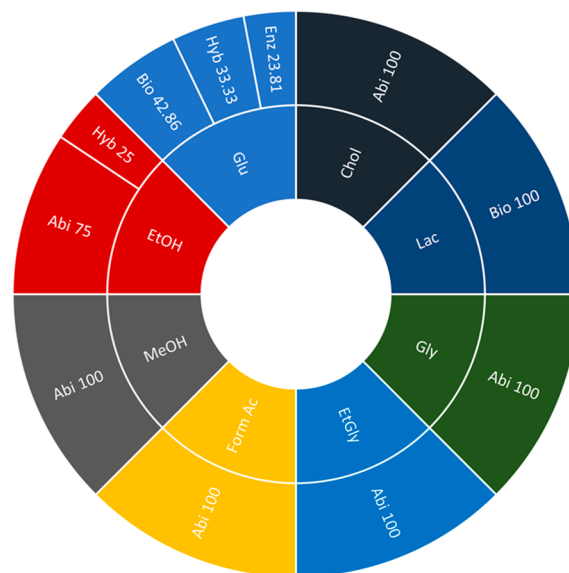


Figure 17. Comparison of fuels and electrocatalyst types for  $\mu\text{FC}$  as reported by the research group. Glu, glucose; Formic Acid, formic acid; EtGly, ethylene glycol; Gly, glycerol; Lac, lactate; Chol, cholesterol; Abi, abiotic; Hyb, hybrid; Bio, biological; numbers are the percentages published with each type of catalyst.

These fuels are cholesterol, formic acid, and ethylene glycol, which account for approximately 26% of the research articles developed. For these fuels, abiotic catalysts such as Cu and Pt/C were used as the anode and cathode, respectively, which work reliably in the developed devices.

In summary, this review highlights the use of different electrocatalysts and proposes a new classification where the materials can be easily compared to other publications in this field. These materials are mainly used for the oxidation of different alternative fuels in  $\mu$ FCs. This proposal focuses on the trend of the most commonly published fuels considering their versatility, economic accessibility, high power density, and application and then classifies the electrocatalyst used per fuel in  $\mu$ FCs according to the same trend. Regarding the type of electrocatalyst, the use of abiotic materials in the anode and cathode for the oxidation of different fuels is noteworthy, followed by enzymatic biocatalysts, which have become very important due to applications where abiotic materials have limitations, as in the case of lactate, where there are only enzymes or hybrids. In the latter case, hybrid catalysts take advantage of both catalytic properties to improve the overall performance of  $\mu$ FCs.

In conclusion, this research group has made a significant contribution to the development of  $\mu$ FCs, particularly in the areas of design, applications, fuels, and electrocatalytic materials, contributing to research at an international level, as described in Figure 17.

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## ABBREVIATIONS

FC	fuel cell
GLU	glucose
MeOH	methanol
ETOH	ethanol
LAC	lactate
GLY	glycerol
KOH	potassium hydroxide
$\mu$ FC	microfluidic fuel cell
nFC	nanofluidic fuel cell
H $\mu$ FC	hybrid microfluidic fuel cell

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