Electrical valorization of MFC : application to monitoring

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1. INTRODUCTION

1.1 Abstract (EN)

In recent years, the extensive use of fossil fuels has triggered a global crisis due to high pollution and resource reduction. The wide use of fossil fuels has led to the production of high amounts of CO_2, as a result is a trigger of the global warming issue.

Microbial fuel cells (MFCs) is an energy harvesting technology that converts chemical energy from organic compounds to electrical energy through catalytic actions of microorganisms. MFC can be considered as an example of archetypical microbial Bioelectrochemical Systems (BESs), that exploit the bio-electrocatalytic activity of living microorganisms for the generation of electric current.

In the past decade, the evolution of low power electronics has made MFCs technology more attractive, because it has become suitable for low-power devices forming complete systems, such as the nodes of a wireless sensor network (WSN). Moreover, MFCs gained more interest because they can generate electric power while treating wastes. Unlike other fuel cells, MFCs can continuously generate clean energy at normal temperature, atmospheric pressure, and neutral pH values without any supplementary maintenance. The only by-products are CO_2 and H_2O, which do not require additional handling. The production of CO_2 is part of the intermediate carbon cycle. The CO_2 produced is biogenic, which is included in the biogeochemical carbon cycle, avoiding net carbon emission into the atmosphere.

This manuscript examines many aspects related to microbial fuel cell technology from chemical reactions inside the cells to the energy management systems required to exploit energy delivered from MFCs for practical usage in autonomous sensors. The line of experiments was performed on MFCs regarding electrical characterization, multiple connections of MFCs and influence of main parameters that affect the energy conversion performance.

The experimental tests were performed on two different lab-scale reactor typologies: terrestrial microbial fuel cell and waste water microbial fuel cell.

A survey is presented about different proposed energy management systems and other devices able to supply a node of a WSN powered by MFCs.

1.2 Abstract (IT)

Negli ultimi anni, l'uso estensivo di combustibili fossili ha scatenato una crisi globale a causa sia degli elevati livelli di inquinamento prodotti sia della riduzione delle scorte, come effetto della sua natura di fonte d'energia non rinnovabile. L'ampio uso di combustibili fossili ha portato alla produzione di elevate quantità di CO_2, con il risultato conseguente del riscaldamento globale. Le celle a combustibile microbiologico (MFC) sono una tecnica di energy harvesting che converte l'energia chimica da composti organici in energia elettrica attraverso reazioni chimiche catalizzate da microrganismi. Le MFCs possono essere considerate come forme archetipiche di sistemi microbici bioelettrochimici (BESs), che sfruttano l'attività bioelettrocatalitica dei microrganismi viventi per la generazione di corrente elettrica. Nell'ultimo decennio, l'evoluzione dell'elettronica a bassa potenza ha reso la tecnologia MFC più attraente, perché ha iniziato ad essere in grado di alimentare dispositivi a bassa potenza formanti sistemi completi, quali i nodi di una rete di sensori wireless (WSN). Inoltre, le MFC hanno acquisito maggiore interesse per la possibilità di generare energia elettrica mentre trattano i rifiuti. A differenza di altre celle a combustibile, le MFC possono generare continuamente energia pulita a temperatura ambiente, pressione atmosferica e valore di pH neutro senza manutenzione supplementare. Gli unici sottoprodotti sono CO_2 e H_2O, che non richiedono ulteriore trattamento, perché la CO_2 prodotta è biogenica, che è inclusa nel ciclo del carbonio biogeochimico, evitando emissioni nette di carbonio nell'atmosfera.

In questa tesi vengono esaminati tutti gli aspetti relativi alla tecnologia delle MFC, dalla reazione chimica che avviene all'interno delle celle ai sistemi di gestione dell'energia necessari per sfruttarne l'energia convertita. Una campagna sperimentale è stata condotta sulle MFCs riguardante la caratterizzazione elettrica, la connessione multipla e l'influenza dei parametri principali sulle prestazioni nella conversione dell'energia.

I test sperimentali sono stati condotti in laboratorio, con la progettazione e realizzazione anche di dispositivi di misura custom, su due diverse tipologie di reattore: cella a combustibile microbiologico terrestre e cella a combustibile microbiologico con acque reflue. Inoltre, nella tesi si indagano i diversi sistemi di gestione dell'energia sostenibile con MFC, finalizzandoli alla progettazione dei nodi di una WSN, realizzati con i più recenti dispositivi low voltage e low power.

1.3 Abstract (FR)

Dans les dernières années, l'utilisation intensive des combustibles fossiles a déclenché une crise mondiale due à la forte production de polluants et à la réduction des stocks, en raison de sa nature de source d'énergie non renouvelable. Parce que l'utilisation généralisée des combustibles fossiles a entraîné la production de grandes quantités de CO_2, ce qui est un facteur aggravant du réchauffement de la planète.

Les piles à combustible microbiennes (MFC) représentent une technique de récupération d'énergie qui convertit l'énergie chimique des composés organiques en énergie électrique par le biais de réactions catalytiques de micro-organismes. La MFC peut être considérée comme un archétypique de système microbien bioélectrochimique (BES), qui exploite l'activité bio-électrocatalytique de micro-organismes vivants pour la génération de courant électrique.

Durant la dernière décennie, l'évolution de l'électronique de faible consommation a rendu la technologie des MFC plus attrayante, car elle commence à pouvoir fournir une énergie comparable à celle consommée par des périphériques dit à faible consommation, comme un nœud de réseau de capteurs sans fil (WSN). En plus, les MFC ont gagné en intérêt car elles peuvent générer de l'énergie électrique tout en traitant des déchets. Contrairement aux autres piles à combustible, les MFC peuvent générer en permanence une énergie propre à une température ambiante, à la pression atmosphérique et à un pH neutre, sans entretien supplémentaire. Les seuls sous-produits sont le CO_2 et H_2O, qui ne nécessitent aucune manipulation supplémentaire, car le CO_2 produit est biogénique, ce qui est inclus dans le cycle du carbone biogéochimique, évitant l'émission nette de carbone dans l'atmosphère.

Ce manuscrit examine certains aspects liés à la technologie des piles à combustible microbiennes, depuis les réactions chimiques jusqu'aux systèmes de gestion de l'énergie requis pour exploiter la puissance fournie par les MFC. Une campagne expérimentale a été menée sur les MFCs concernant la caractérisation électrique, la connexion multiple des MFCs et l'influence des principaux paramètres qui affectent les performances de conversion de l'énergie.

Les essais expérimentaux ont été effectués sur deux types de réacteurs : la pile à combustible microbienne terrestre et la pile à combustible microbienne à eau usée. Une enquête est menée sur différents systèmes de gestion de l'énergie proposés et sur d'autres systèmes de gestion de l'énergie capables de constituer un nœud de réseau WSN alimenté par des MFC.

1.4 Energy harvesting techniques

The reduction of energy required by electronic devices, allows the use of clean renewable sources with low power generation. In fact, energy harvesting technologies have become increasingly popular. They are based on energy conversion from a primary energy source harvested from the environment, such as: chemical [36], solar thermal [11], vibrational [4], Radio Frequency (RF) [123] or/and natural flow of water [83].
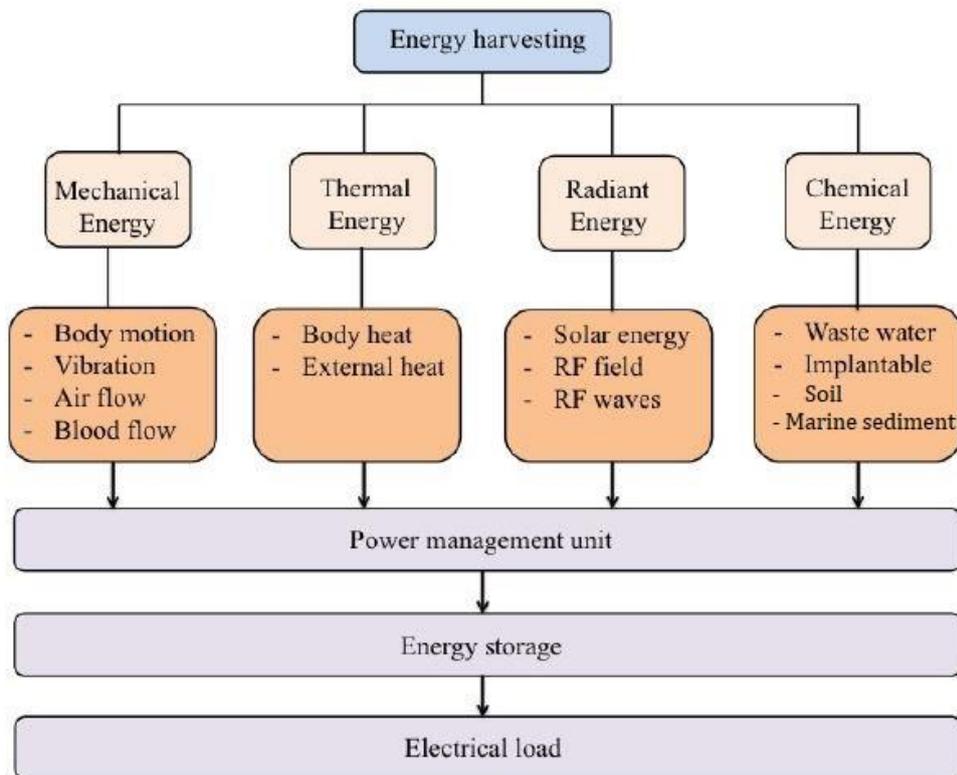
Fig 1.1: Various energy harvesting techniques

It is possible to regroup the various energy harvesting techniques in four main fields: thermal, radiation, mechanical and chemical energy as shown in Fig. 1.1.

Available ambient energy could be harvested, converted into usable electrical energy, stored and used for many purposes depending on energy production, from systems that required high power values to small scale electronics and low-power devices, for applications such as wireless monitoring and mobile electronics.

Small-scale energy harvesting techniques from ambient energy (such as vibrational, thermal, chemical, RF, etc.) are receiving increasing attention. The improvements in low power design and CMOS technologies have led to the development of many micropower electronic applications. Energy harvesting presents thus an important role for alternative low power technology as it can reduce the dependency on batteries which have a number of limitations.

Among limitations of batteries, there's the possibility of complete discharge that brings negative consequences (for the battery and with respect to safety-critical systems) and the fact that batteries contain chemical materials which are hazardous both to the environment and to public health if not carefully handled.

Moreover, batteries have limited lifetime: it means that a battery replacement will be needed. It leads to service disruptions during battery replacement and maintenance costs, especially when the system contains many electronic devices or is in inaccessible zone. Otherwise, rechargeable batteries have a high cost usually.

Furthermore, the size of the batteries can often exceed that of the system components in the electronic device. Usually, batteries are non-operational in exceptional environmental conditions.

So, alternative energy production methods based on harvesting or scavenging, to help design energy-autonomous systems is needed. Internet-of-Things is calling for such solutions. In certain conditions, the microbial fuel cell is a strong candidate.

1.5 Context of Biofuel cell

Biomass is the totality of living or dead organic substances, of vegetable or animal origin. It can come from different environments such as agricultural, aquatic and forest.

It can also come from wastewater, livestock effluents or even waste generated by industries and cities. This organic material is always made up of carbon elements whose chemical bonds prove to be a potential energy reservoir.

This energy can be recovered by combustion, thus converting this chemical energy into thermal energy, which can itself be converted into electrical energy. In addition, biomass can be transformed into biogas (like methane) or biofuel (like ethanol) through various processes as fermentation, digestion, pyrolysis, etc. The product of these reactions can then be converted to electricity by combustion as before. However, combustion processes are generally not without environmental impact .

A fuel cell is a system capable of transforming directly electrical energy from chemical energy without an intermediate step of energy conversion. This process of energy conversion is based on the electrochemical transformation of a chemical substance by oxidation and reduction processes.

As a matter of fact, a combustion is also an oxidation-reduction process, in an MFC this process is controlled by the electron flow in the electrical circuit.

Biofuel cell are electrochemical systems that convert the energy available in biomass directly into electrical energy through the spatial separation of chemical reactions belonging to the same oxidation-reduction pair.

These reactions require the presence of catalysts as chemical, enzymatic or bacterial to increase their natural kinetics. In point of fact, life forms, as microorganisms from mitochondria to microbe, can be exploited as catalysts to perform these transformation processes.

So, organic substances and microscopic living beings can therefore be exploited in a complementary and sustainable way to harvest electrical energy.

1.5.1 Enzymatic fuel cell

These cells use enzymes to catalyse reactions and perform the energy transformation. Glucose fuel cells are an example of these. The enzymes can be extracted or synthesized. The current and power densities obtained by these redox proteins are often higher than those obtained by MFCs. In the case of these bioelectrodes (enzymatic electrodes), the diffusion of the substrates is facilitated compared to the microorganism electrodes, such as bacteria or yeasts. Thanks to the absence of a biofilm and cell membrane and considering that the enzymes are specific for their substrates, in some cases they permit the removal of the separating membrane [67] between the two bioelectrodes, unlike other types of fuel cells. Nevertheless, their stability depends greatly on the immobilization of the enzymes on the surface of the electrodes. The biocatalyst charge is not renewed within the bioelectrode, which leads to a limited stability over time. As a result, they are currently suffering from a short lifespan (7-10 days) [84], which limits their long-term use and applications compared to MFC.

1.5.2 Mitochondrial fuel cell

This new category of bioreactors uses whole organelles as catalysts. In cell biology, an organelle is a specialized subunit within a cell that has a specific function, vital for the life of the cell. There are many types of organelles, particularly in eukaryotic cells. Eukaryotic cells have a nucleus enclosed within membranes, unlike prokaryotes (as bacteria and archaea). The mitochondrion is a double-membrane-bound organelle found in most eukaryotic organisms. Mitochondrial fuel cell use mitochondria as catalysts. These mitochondria present in eukaryotic cells are composed of enzymes and coenzymes that will be able to oxidize biofuels. Just like enzymes, these cannot reproduce, unlike bacteria in microbial fuel cell. This will therefore affect their stability.

1.5.3 Microbial Fuel Cell

The microbial fuel cell recovers the chemical energy of organic matter through the metabolism of certain bacteria to produce electrical energy. These reactors use micro-organisms as catalysts. They are also of interest because of their potential longevity. In addition, these fuel cells make it possible to directly convert biomass into electricity, without requiring a pre-transformation by fermentation or any other chemical process. The energy present in biomass, although very abundant, is still very largely under-exploited due to the lack of suitable technology.

Microbial Fuel Cell is an energy harvesting technology now well introduced in literature [24, 36, 38, 43, 108, 114, 127, 132, 137].

MFCs are based on the simple principle of the circulation of electrons between the anode, where an oxidation reaction catalysed by microorganisms will occur, a loss of one or more electrons, and the cathode, where a reduction reaction of an oxidant takes place, with an electron gain. These two reactions, oxidation and reduction then allow the flow of electrons when the two electrodes are connected by an external circuit. The electrode material also plays an important role as it must be stable enough to keep on the reaction. So, in Microbial Fuel Cell the microorganisms have the role of biocatalyst.

The microbial fuel cell technology offers a way to develop this energy and thus allow the autonomous power supply nodes of a wireless sensor network. It can permit monitoring of rural, marine or urban areas as well as factories or treatment plants that needs distributed and self-powered sensors.

In fig 1.2 was shows the interrelationship occurring in MFC between operating condition, input parameters and output power delivered [29].
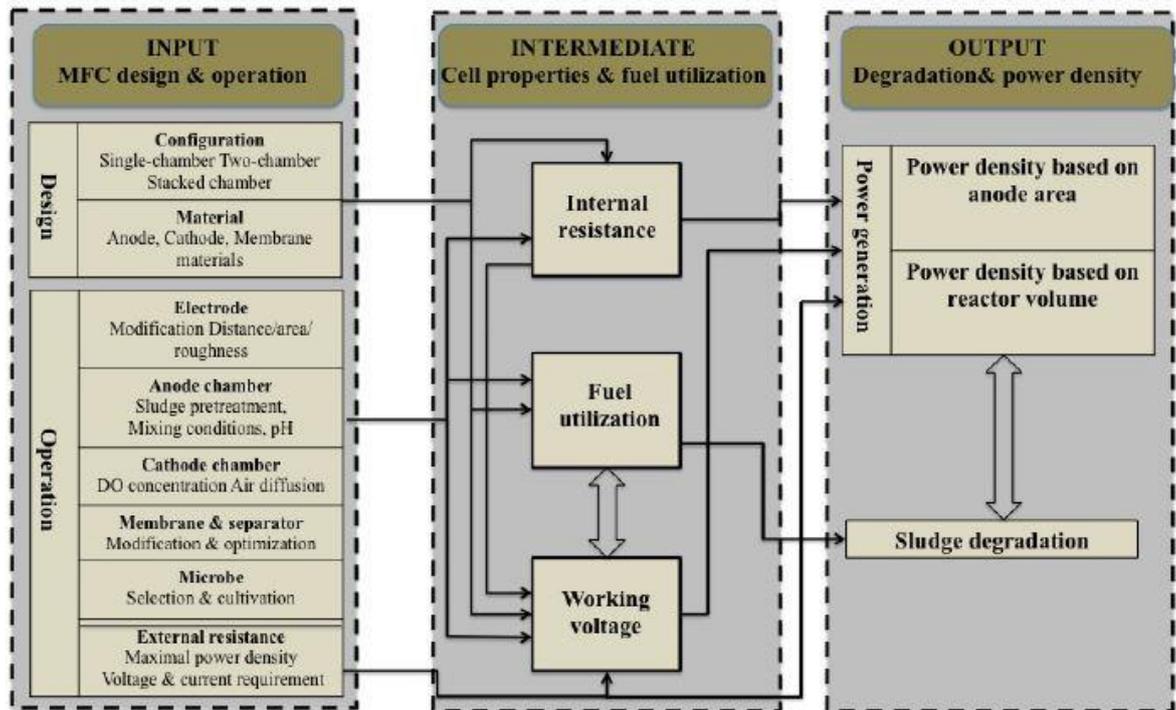
Fig. 1.2: Relations between operating condition, main parameters and power generation in microbial fuel cell [29]

1.6 Bioelectricity and a brief history of MFC

The bioelectricity obtained from the work of microorganisms has been known since the beginning of the last century but has received renewed attention only recently.

In 1791 the bioelectric phenomenon had been observed first from Luigi Galvani [37]: he is considered a pioneer of electrochemistry and bioelectricity. In a famous experiment, he discovered that the muscles of dead frog legs moved when struck by an electrical spark and coined the term "animal electricity" to describe the force that activated the muscles of his specimens as being generated by an electrical fluid that is carried out to the muscles by the nerves.

In 1839, Grove and Schoebein built the first hydrogen-dioxygen fuel cell. This H_2-O_2 battery system attracted the attention of NASA in the 1960s for electricity generation in orbital vehicles. The hydrogen fuel cell is extensively studied today.

In this case, the hydrogen plays the role of fuel and is oxidized at the anode to produce protons (H_+) and O_2 is the reduced oxidant at the cathode to produce water. Protons provide transport through membranes.

In 1911, Potter observed that *Escherichia coli* bacteria produced electricity. It was then shown that many common bacteria produce electricity by natural catabolism of sugars, that is, by degradation of some organic molecules by releasing electrons that can be recovered by the anode of the cell [100].

In 1983, Bennetto added electron mediators to enhance the yield of these bacterial cells. He monitored the electrical effects associated with fermentation in a galvanic cell based on platinum wires and a pure culture of yeast, developing the first bio-based battery [6].

In 1999, the first report was published that species *Shewanella* could transfer electrons directly in mediator-less microbial fuel cells [59][60]. It led to eliminate the mediator in MFCs. An improvement that was attributed to the minimized distance between the electrode and bacteria, that a mediator had to travel. Consequently, the distance between electrodes of the MFC was minimized. This design exhibits improved electrical performance of reactors.

The research on MFCs field of fundamentals, methods and materials started to have contributions from material science, environmental engineering, electrical engineering, electronics, biology, microbial physiology and electrochemistry in the course of new century. This has recently made the study of MFCs truly interdisciplinary. As a matter of fact, this kind of research invests many science fields and requires a strong interconnection of knowledge following interdisciplinary paths.

2. MICROBIAL FUEL CELL

2.1 MFC principles

A microbial fuel cell is a bioreactor that turns energy stored in chemical bonds of organic compounds into electrical energy. The cell is generally composed of two chambers, one anode and one cathode, each of which includes an electrode. There are some types of reactors that combine the two chambers in one [33].

In the anode chamber, under anaerobic conditions and in a nutrient-enriched environment, the organic matter oxidized into carbon dioxide by microorganisms, produces electrons by means of an equivalent reduction operation (Fig. 2.1). These charges are transferred to the cathode through an external circuit connecting the electrodes and a simultaneous generation of protons, which are then passively transferred to the cathode electrode. The protons, transferred to the cathode chamber in aerobic condition, react together with oxygen to form water molecules.

A semipermeable Proton Exchange Membrane (PEM) can divide the two chambers to ensure the transfer of protons. The proton exchange membrane allows the transport of positively charged ions (protons) from the anode to the cathode, thereby maintaining pH and electro-neutrality and blocks the migration of oxygen.
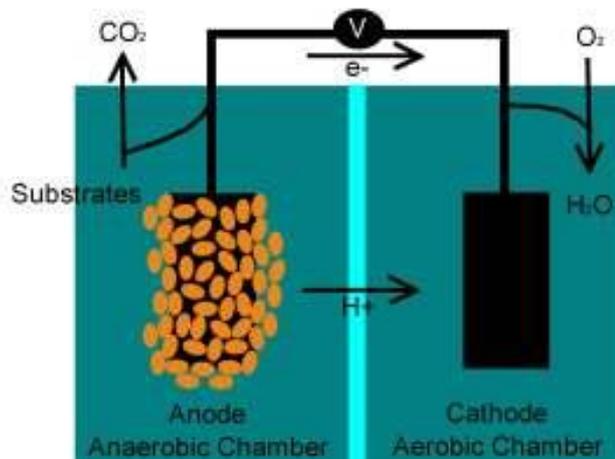
Fig. 2.1: Microbial fuel cell basic principles

An MFC can be in double-chamber or single-chamber configuration. In a single chamber MFC design, the proton exchange membrane is either removed or pressed against the anode or cathode to form Membrane Electrode Assemblies. Indeed, a simpler design where the proton exchange membrane could be eliminated will offer more perspective for energy harvesting. It is the case of reactor configuration as Terrestrial Microbial Fuel cell (TMFC) lab-scale.

A double-chamber MFC is composed of two compartments separated by an Ion Exchange Membrane (IEM) which can be either a proton or a cation exchange membrane. The anodic compartment contains the organic substrate and the bacteria, whereas the cathodic compartment contains an electrolyte rich in electron acceptor (oxygen).

A single-chamber MFC is composed of an anodic compartment alone. The cathode is merged with the reactor such that it interfaces the internal electrolyte and the external air. A membrane can be placed on the internal side of the cathode to limit the diffusion of oxygen within the reactor.

The basic advantage of exposing the cathode directly to air is to eliminate any limitation in oxygen supply to the electrode due to mass transport issues. These modifications minimize the internal resistance and increase the power generation [76]. The main advantage of this type of MFC is that it does not require any aeration of the cathodic electrolyte, reducing thus the hydraulic flow. This design is more suitable for large geometry scale and wastewater treatment [69].

The single-chamber configuration has been used for the Waste Water Microbial Fuel Cell (WWMFCs) lab-scale reactors.

Acetate is commonly used as substrate in MFC. Acetate is an organic anion, a negatively electric ion. It is the strong conjugated base of *acetic acid*, an organic molecule very common in living systems and widely used in industry and in the chemical laboratory. The chemical formula of Acetate is CH_3COO^-.

Acetic acid, also named ethanoic acid, is a colourless liquid organic compound. Its chemical formula is CH_3COOH.

In detail, it is possible to observe the reactions occurring within a cell using *acetate* as substrate[76]:

Anodic reaction: $CH_3COO^- + 4H_2O \longrightarrow 2CO_3^- + 9H^+ + 8e^-$ (1)

Cathodic reaction: $2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O$ (2)
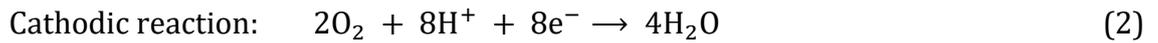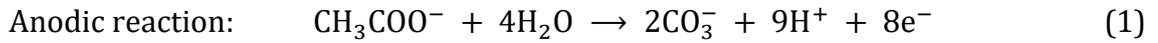
The carbon dioxide is generated as a product of oxidation. However, there are no net carbon emissions into the atmosphere, because the CO_2 produced is biogenic, which is included in the biogeochemical carbon cycle.

Compared to traditional inorganic fuel cells, which use energy generated from fossil fuel conversion, an MFC bases its operational mode on biofuel and biocatalyst as the essential elements: they therefore represent a sustainable zero emissions technology. The only parts that could be not nature-based, may be some MFC construction materials and any electronic components necessary for its operation. It is out of the scope here, but net balance of energy is in favor of MFCs. The energy balance, as the embodied, is a retrospect figure at the end of life of an electricity generator to verify if the total amount of energy produced is higher than the energy necessary to build the system (ecological impact is also converted in energy). An MFC could work a very long time, as the electronic part is not submitted to electro-thermal stress. The electrical performances are low, but the degradation of waste(even polluting waste) is a favorable add-on that correct in a positive way the energy balance.

Microorganisms are the **biocatalysts** used in this technology because of both their wide abundance in the biosphere and the ability to self-sustain of some microbial species. Particularly for the latter feature, the production of energy by an MFC is continuous, and it is limited only by the availability of nutrients within the anode support.

The **transfer mechanism of electrons** into the cell can occur in three different ways (fig. 2.2):

1) direct transfer from the molecule to the anode surface;
2) transfer of electrons through external mediators, employing a secondary biomolecule that carries electrons to the anode (e.g., *Pseudomonas aeruginosa*, which produces the pyocyanin);
3) electron transfer through bacterial appendages, named nano-wires.
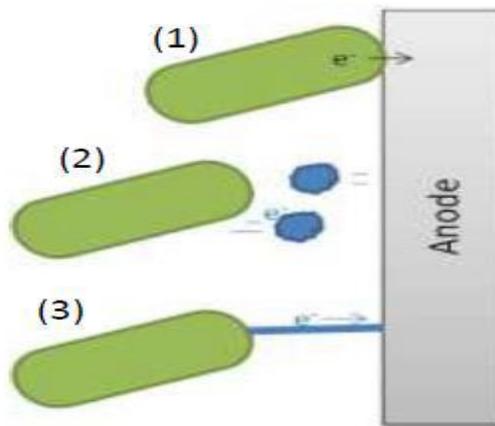
Fig 2.2: Three different ways of transfer mechanism of electrons into MFC

When a microbial community forms and begins to respire at the anode surface, the highly reduced biomolecules start to accumulate around the anode. This build-up of metabolic by-products decreases the electrical potential of the anode, settling on values typically between −0.4 V and −0.1 V *vs.* SHE (Standard Hydrogen Electrode).

The presence of oxygen moves the electrical potential of the cathode to a higher value, typically from 0.4 V to 0.8 V *vs.* SHE. The working voltage of the MFC is merely the potential of the anode subtracted from the potential of the cathode. It should be noted that MFCs have a theoretical maximum voltage, approximately 1.2 V between the two electrodes, since the redox potential of reduced biomolecules has a minimum of around −0.4 V *vs.* SHE and the redox potential of oxygen is 0.8 V *vs.* SHE [23].

However, the laboratory performance of MFCs is usually lower than the ideal performance. The energy converted in an MFC is a function of numerous factors, such as the possible geometries of the system and the types of involved bacteria.

The main operating parameters influencing the overall performance of MFC systems are: pH and temperature, which directly influence the microbial metabolic activities; the water content in Terrestrial Microbial Fuel Cell, which influences the diffusion of both the nutrients and of the protons, the type and concentration of biomass and substrate used, the electrode materials and its surface area.

The MFC typologies as TMFCs, WWMFCs and Benthic Microbial Fuel Cells (BMFCs) are influenced by these parameters in different way: it was tested the influence of pH and temperature and substrate concentration on MFC. The temperature plays an important role for WWMFCs and the pH value of soil is important for TMFCs.

In WWMFC, it is possible to consider also the waste water/sludge degradation as an output of the system. Considering that the total organic carbon (TOC) present in an organic substrate inside a water solution generally decaying over time (not inside soil), if the solution is feeding a WWMFC it happens faster than usually. So, the cell can clean the water from organic carbon or other specific compounds the same time as it produces energy.

2.2 MCF operation and main application

Microbial fuel cell can be viewed from different perspectives other than an energy source. It can be considered as a *Bio-fuel cell*, *Bio-sensor* and *Bio-decontaminators* with different and wide application fields.

2.2.1 Bio-fuel cell

Microbial fuel cell can be exploited in terms of *Bio-fuel cell* as clean power source useful to supply low power electronics devices able to empower a node of a wireless sensor network for environmental and agricultural monitoring.

Also, MFCs arranged in the form of a cluster to be use as a small power plant allow more complex applications like the chance to supply energy independent robots and drones.

2.2.2 Bio-sensor

A biosensor is a device that combines microorganisms with a transducer to produce a measurable signal such as voltage or current intensity proportional to parameters such as substrate concentration. An example of transducer is like Bioluminescence used as biosensors [107].

MFCs can be used to report, through the monitoring of the energy produced, the evolution of an environmental parameter. A variation of a parameter corresponds to a variation of voltage or current signal delivered by the bioreactor.

Therefore, it is possible to use an MFC as a *bio-sensor*, for example to measure values as pH, temperature, *biological oxygen demand* or also called *Biochemical Oxygen Demand* (**BOD**) [53][87], which makes it possible to evaluate the organic pollution of a water), *Chemical Oxygen Demand* (**COD**) [25] or water quality monitoring [14][79]. Biosensors based on MFCs can suffer from the low sensitivity because of the low power generated by MFCs.

The **BOD** is a measure of the oxygen amount required by bacteria to degrade the *organic* components present in water/waste water. It is a measure of the capacity of organic matter to consume oxygen.

The BOD removal rates are indicators of how fast the organic matter is consumed. It is directly linked to the reaction rate and as such to the output current.

Instead, **COD** or Chemical Oxygen Demand is the total measurement of all chemicals (organics & in-organics) in the water/waste water. The COD removal rate represents the consumption of all organic and inorganic matter.

The COD effectively is a measure of the number of electrons available in the organic carbon for reduction of oxygen to water. TOC is the amount of total organic carbon. The ratio is therefore a measure for the degree of reduction of the carbon compounds.

BOD is similar in function to COD, in that both measure the number of organic compounds in water. However, COD is less specific, since it measures everything that can be chemically oxidized, rather than just levels of biodegradable organic matter.

The most common application of COD is in quantifying the amount of oxidizable pollutants found in surface water (e.g. lakes and rivers) or wastewater. COD is useful in terms of water quality sensing by providing a metric to determine the effect an effluent will have on the receiving body, much like BOD.

The quality of wastewater generated in any industrial process is generally indicated by performance indices namely BOD, COD and TOC, expressed in mg/L. The use of TOC as an analytical parameter has become more common in recent years especially for the treatment of industrial wastewater.

2.2.3 Bio-remediator

Microbial fuel cell as *bio-remediator* offers the possibility to decontaminate polluted soils or wastewater by chemical degradation in addiction to convert at the same time the chemical energy of organic materials presents inside soils and wastewater into electricity by the metabolism of bacteria.

In the context of water treatment, pointing the decontamination of certain compounds, an example is the Shortcut Biological Nitrogen Removal (SBNR) using wastewater microbial fuel cell [3] or the bioremediation of Polycyclic Aromatic Hydrocarbons (PAHs) [119].

In [3], a short removal of *nitrite* and *nitrate* was observed when fumaric acid was used as organic carbon source with acetate.

The efficiency of a WWMFC can be improved in Waste Water Treatment Plants (WWTPs) using wastewater rich in organic matters such as sanitary wastes, food processing wastewater, swine and corn stove wastewaters. MFC can also be used to produce bio-hydrogen instead of electricity.

2.3 Bacteria involved in MFCs

The most interesting class of bacteria is one that can produce electricity without requiring the addition of mediators. Known as *electroactive* species, these bacteria directly transfer electrons to chemical species or a substance that is not an immediate electron-acceptor. Among the major strains of electroactive bacteria, can count *Geobacter metallireducens*, *Geobacter sulfurreducens* [10] and *Desulfuromonas acetoxidans* in the family of *Geobacteraceae*, while among *Shewanella*, we mention *Shewanella putrefaciens* [60] and *Shewanella oneidensis* [39].

The MFC voltage is determined by the difference in redox potential between the two distinct electrodes. Redox potential discloses the tendency of a chemical species to be reduced that is to acquire electrons. Its value is expressed in volt (V).

Many MFC researchers are evaluating the benefits related to the inoculation of certain species of electroactive bacteria. However, for MFCs that use natural substrates such as soil, sediments or effluents, inoculation is not necessary, since these species of electroactive bacteria are already present in abundance, along with complex sugars and other nutrients that have accumulated during millions of years due to the decay of plants and material of animal origin.

The current research has not yet given results regarding the existence of an isolated bacterial strain able to guarantee a higher energy production compared to that obtained from other strains or compared to mixed cultures.

Identifying a potential strain capable of ensuring higher current densities and understanding the synergy or antagonism taking place between different bacterial strains is the goal of current research.

The following table in Fig 2.3 shows some of the bacterial strains that have been identified in literature within the substrates used in MFCs.

Microbes	Substrate	Applications
Actinobacillus succinogenes	Glucose	Neutral red or thionin as electron mediator
Aeromonas hydrophila	Acetate	Mediator-less MFC
Alcaligenes faecalis, Enterococcus	Glucose	Self-mediate consortia isolated from MFC with a maximal level of 4.31 W m−2.
gallinarum, Pseudomonas aeruginosa	Starch, glucose,	Fermentative bacterium
Clostridium beijerinckii	Starch, glucose,lactate, molasses	Fermentative bacterium
Clostridium butyricum	Starch, glucose,lactate, molasses	Sulphate/sulphide as mediator
Desulfovibrio desulfuricans	Sucrose	Ferric chelate complex as mediators
Erwinia dissolven	Glucose	Ferric chelate complex as mediators
Escherichia coli	Glucose sucrose	Mediators such as methylene blue needed.
Geobacter metallireducens	Acetate	Mediator-less MFC
Geobacter sulfurreducens	Acetate	Mediator-less MFC
Gluconobacter oxydans	Glucose	Mediator (HNQ, resazurin or thionine) needed
Klebsiella pneumoniae	Glucose	HNQ as mediator biomineralized manganese as electron acceptor
Lactobacillus plantarum	Glucose	Ferric chelate complex as mediators
Proteus mirabilis	Glucose	Thionin as mediator
Pseudomonas aeruginosa	Glucose	Pyocyanin and phenazine-1-carboxamide as mediator
Rhodoferax ferrireducens	Glucose, xylose, sucrose, altose	Mediator-less MFC
Shewanella oneidensis	Lactate	Anthraquinone-2,6-disulfonate (AQDS) as mediator
Shewanella putrefaciens	Lactate, pyruvate, acetate, glucose	Mediator-less MFC but incorporating an electron mediator like Mn(IV) or NR into the anode enhanced the electricity production
Streptococcus lactis	Glucose	Ferric chelate complex as mediators

Fig 2.3: bacterial strains identified within the substrates used in MFCs [104]

Some studies have shown, for example, that the use of pure cultures can facilitate the formation of electroactive biofilms and, therefore, allow the achievement of better performance. In another researches, the use of complexes of mixed cultures allows the use of the substratum in a much wider way since, in an MFC with mixed cultures, there are both electroactive groups and groups that use natural mediators [47].

However, it must also be kept in mind that a high value of the internal resistance of the cells does not allow high current production.

From this point of view, a future research will therefore be the evaluation of the convenience of cultivating isolated bacterial strains, favoring mixed cultures or rather concentrating the interventions on improving the intrinsic characteristics of the cell.

2.4 Different typologies of Microbial fuel cell

There are different typologies of microbial fuel cells, depending on reactor configuration, membrane and substrates used. One is named the terrestrial microbial fuel cell and is founded on the same basic MFC principles described above; whereby, standard topsoil is the nutrient-rich anodic medium, the bacteria inoculum and the proton-exchange membrane. Another type of bioreactor is the waste water microbial fuel cell where waste water acts as flow of nutrient and bacteria. Moreover, there are some different types of MFCs, like benthic or plant MFCs.

2.4.1 Benthic Microbial Fuel Cell

Benthic microbial fuel cells (BMFCs) are MFCs that recover energy from marine sediments. BMFCs can be deployed in all types of aquatic environments with a carbon-rich substrate where electroactive bacteria can grow and proliferate.

In the case of the BMFC (Fig. 2.4), the sediment is related to the anode compartment and the supernatant water (on the sediment surface) to the cathode compartment.

The naturally created interface between water and sediments play the role of the proton exchange membrane. This interface thus passes ions and filters oxygen present in the water. This filtration is even more effective because some of the bacteria present in the anodic chamber are aerobic, i.e. they consume oxygen. With a sufficiently deep immersion of the electrode (a minimum of few centimeters), the anode compartment is therefore assumed to be anaerobic.

Oxygen dissolved in water comes from both surface oxygen that diffuses into the surface layers and photosynthesis from nearby plants. The distribution of this oxygen is ensured by the continuous flow of water thanks to the waves and the wind.

The layers close to the surface are thus generally saturated with oxygen. In addition, the ocean floor has a very rich and diverse bacterial flora among which electro-active bacteria necessary for the functioning of the BMFC.

Moreover, it is full of organic matter resulting from animal, plant and bacterial degradation, accumulated and constantly renewed.

Finally, although it is accepted that the rate of oxygen in the water decreases with depth, it has been shown that the continuous flow of water ensures a circulation of (free) oxygen, enough to maintain a good operation of the cathode about 1 km deep [91].

This perfusion of fuel thus lends the Benthic microbial fuel cell a potentially infinite lifespan.
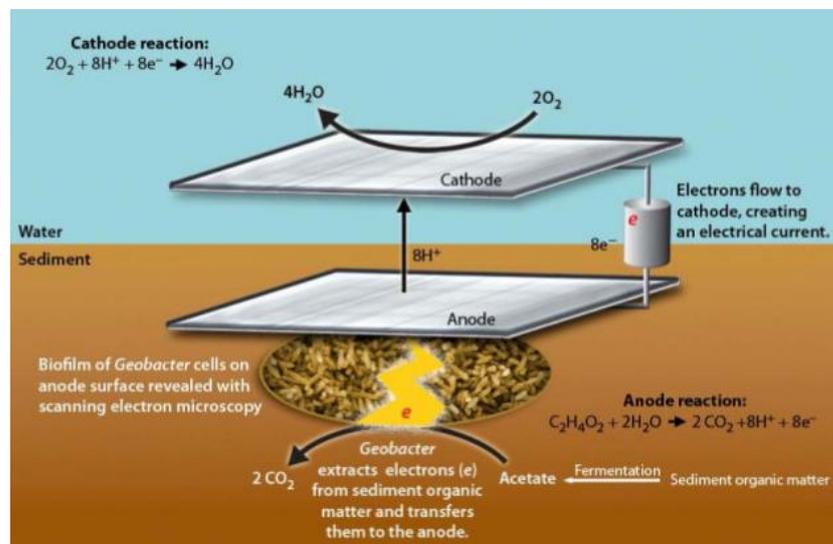
Fig 2.4: Typical operation of a Benthic Microbial Fuel cell [9]

In the case of benthic microbial fuel cells, ocean sediment acts as the nutrient-rich anodic media, the inoculum and the proton-exchange membrane the anodic redox potential typically leveling at approximately −0.4 V vs. SHE and the cathode may still exhibit a potential of 0.4 V vs. SHE at depths in excess of 950 meters [40]. Generally, the anodic redox potential could be up to -0.54 V (oxidation of CO_2/Acetate) and the cathodic redox potential could reach +0.56 V (reduction O_2/H_2O) for a maximum voltage between electrodes of 1.1V [13].

BMFCs can be useful for a wide range of applications and are particularly advantageous in areas that are difficult to access, such as deep water, where devices need to be installed over long periods and fed intermittently, where battery replacement and regular maintenance are problematic.

These BMFCs were able to feed sensors for various purposes, as sensors for water monitoring, climatic and pollution control and as submarine magnetometer to detect the passage of boats. So, a WSN powered by BMFCs can perform marine environment monitoring from boat traffic control and security [5] to water monitoring and disaster prevention. Furthermore, BMFCs can be exploited in many environments over sea, including rivers, to power a wider variety of sensors. Moreover, naval warfare research departments are taking increasing interest in this technology, due to its applications in naval traffic monitoring from boats to submarines [5].

2.4.2 Terrestrial Microbial Fuel Cell

The terrestrial microbial fuel cell (TMFC) is founded on the same basic MFC principles described above; whereby, standard topsoil is the nutrient-rich anodic medium, the inoculum and the PEM.

As a matter of fact, it is possible to harvest energy from the soil present in the entire earth using proper electrodes, in any moment everywhere and forever.

Microbial fuel cells in configurations such as BMFC or WMFC must work principally in a marine environment or in presence of waste water, which limits the MFCs' application fields. Terrestrial microbial fuel cells can be inoculated by soil or even work on land, which can overcome the disadvantages and extend the MFCs' application range. TMFC can be used as a closed reactor with a controlled environment able to self-maintain its functioning for years or installed directly on a land with or without presence of plants.

In a terrestrial microbial fuel cell (Fig. 2.5), the anode is placed at a working depth, generally about 8 cm into the ground, while the cathode is preferable on top of the soil, in order to expose it to the oxygen in the air.

In the classical configuration the two electrodes, the anode and the cathode, of an MFC are made of graphite felt. Besides being an appropriate conductor, graphite is also a very economical material.

Located in the soil, the aerobic microbes act as an oxygen filter, consuming oxygen and, thus, preventing infiltration into the anode compartment.

Also, microbial communities that degrade the nutrients present and trigger the reactions necessary for the generation of energy.

One of the main advantages of TMFCs is that it does not require the use of a semi-permeable cation exchange membrane, usually made of very expensive materials. As a matter of fact, the aerobic microbes, naturally contained in the ground, which behave like a filter, consuming oxygen and thus preventing infiltration into the anodic compartment. At the same time the soil, having its own electrical conductivity, allows the migration of hydrogen ions to the cathode.
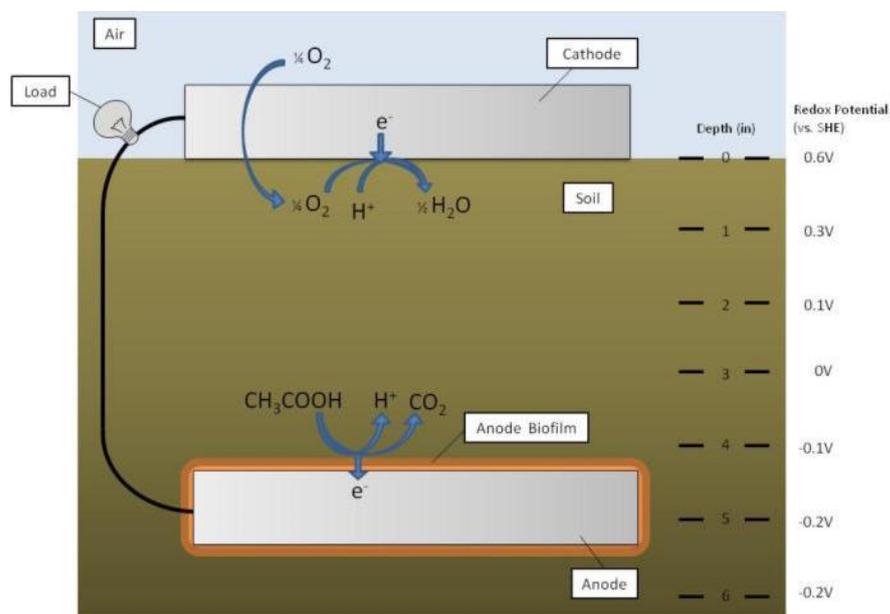
Fig. 2.5: Main operation of a TMFC

The typical electrical potentials achieved in TMFCs are 0.2 V to 0.6 V vs. SHE for the cathode and in a range from −0.2 V to 0.0 V vs. SHE for the anode [23]. Therefore, the theoretical maximum voltage of TMFC that can be achieved between the two electrodes is approximately 0.8 V.

Another typology of MFC is *plant microbial fuel cell* (PMFC), where living plants transport substantial amounts of organic material into the soil. The release of organic compounds from plant roots into the surrounding environment, called rhizodeposition, provides the substrate for the rhizospheric microbial community.

An example is an MFC planted with rice, which can reach open circuit voltage (OCV) of 0.8 V with an anodic redox potential of −0.34 V vs. SHE. [116]

2.4.3 Waste Water Microbial fuel cell

The waste water fuel cell (WWMFC) is equally based on the same basic MFC principles, where the waste water plays the role of flow of nutrient (*biofuel*) and inoculum of bacteria (*biocatalysts*) [132]. These cells are generally is single-chamber configuration (Fig. 2.6). The chamber is filled with waste water and the anode is placed inside water. Usually, an air-cathode is used for WWMFCs, which is useful to eliminate any limitation in oxygen supply to the electrode due to mass transport issues.

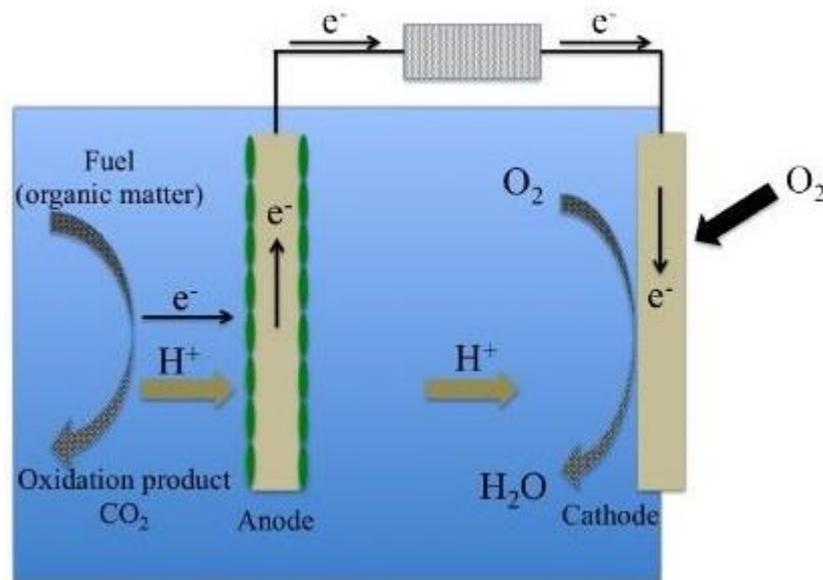*Fig. 2.6: Scheme of a single-chamber MFC*

2.5 Continuous flow and batch mode

There are different possible operation modes for a WWMFC, under *continuous flow* or in *batch* mode [92], and also *semi-continuous*, *semi-batch* and *re-circulation* mode.

When a microbial fuel cell is in *continuous flow* operation, it means that it is under continuous feeding conditions. Therefore, a hydraulic connection is needed between the reactor and a waste water source, so the water solution keeps flowing in the reactor and feeding it.

Otherwise, a microbial fuel cell under *batch mode*, is a closed reactor filled with a water solution, which remains in the reactor without being modified but can be recirculated. The lack of a continuous flow, besides not continuously providing a renewed fresh waste water, leads the reactor to suffer from substrate sedimentation phenomena at the bottom of the cell, making the process less efficient due to the reduced available substrate. Also, the organic substrate decays faster. Recirculation overcomes the latter issue but necessitates a pumping effect, that requires the production of electricity (consumption).

Moreover, a *fed-batch mode* is possible [72], often conducted by adding a fresh dose of substrate when the electrical output falls below a baseline, or by replacing the whole solution or a part of the solution. Fed-batch mode is being the most common practice so far for laboratory works [114].

The effect of fed-batch vs. continuous mode of operation on microbial fuel cell performance treating biorefinery wastewater was analysed in [92], the fed-batch MFC achieved a similar current density of continuous flow mode, however, its performance dropped significantly after 36 days of operation due to substrate degradation. In comparison, anode conversion efficiencies of the continuously-fed MFC remained almost stable after 48 days of operation. In [103], a dual chamber configuration MFC fed by glucose attained the highest obtained voltage of 760 mV in batch system and it was stable for duration time of 72 h. The WWMFCs lab-scale are operated in batch and fed-batch mode for the experiments, also monitoring the substrate concentration role and substrate degradation effect on MFC efficiency.

2.6 Substrates

The substrate has an important biological factor affecting the performance and the electricity generation. Different substrates have been used in MFCs ranging from pure compounds to complex mixtures of organic matter [65].

All organisms can be classified in base of their primary *source of carbon* and their primary *source of energy*. For heterotrophic organisms, organic compounds are metabolized to get carbon for growth and development. For autotrophs organism instead, the carbon dioxide (CO_2) is used as source of carbon.

A heterotroph is an organism that relying on the intake of nutrition from sources of organic carbon, mainly plant or animal matter.

Heterotrophs may be subdivided according to their primary *energy source*, if the heterotroph uses chemical energy, it is a *chemotroph*. Instead they are called *phototroph* if they use photosynthesis to acquire energy (sunlight energy). All animals (herbivores, carnivores and omnivores) are chemoheterotrophs (meaning they oxidize chemical compounds as a source of energy and carbon), as are fungi, protozoa, and some bacteria.

Chemotrophs bacteria are the most interesting. They oxidize chemical substances with their respiratory organisms and in the presence of electron acceptor, such as oxygen, this reaction releases energy. When the oxidation and reduction reactions in the respiratory mechanisms can be separated, can be harvested a part of the energy available from these reactions.

Chemotroph organism are called *chemoorganotrophs* when their energy source (electron donors' molecules) are organic or *chemolithotrophs* for inorganic.

These *chemoorganotrophic* bacteria are capable of oxidizing a wide variety of organic molecules (substrates) by producing useful energy for their growth and maintenance of their metabolism. The substrate then serves for the bacteria as a source of carbon and energy.

The *substrates* used by biofilms can be any kind of organic matter from simple molecules (as glucose, acetate, carbohydrates) to complex compounds (as cellulose, composed of many glucose molecules) as well as the organic matter

contained in the wastewater treatment plants, agricultural, animal and domestic wastes and any type of fermentable substrates. Acetate and glucose are two common typologies of substrates utilized in MFCs.

The efficiency of the bioelectrochemical conversion of the organic substrate into energy depends on composition, characteristics and concentration. The nature of the substrates affects the composition of bacterial populations that grow within the biofilms, but also the bioelectrochemical performance, in the term of current density or the coulombic efficiency of bioanodes.

In most of the MFC studies, acetate has been chosen as substrate for electricity generation [71]. Acetate is a simple substrate, an intermediate product which appears in many oxidation reaction chain. Also, it is used as carbon source to induce electroactive bacteria. It was reported that using acetate in a single-chamber MFC offers a maximum power density of 506 mW/m2 at 0.8 g/L, compared to 305 mW/m^2 at 1 g/L produced with butyrate [71].

Glucose is also a commonly used substrate in MFCs [134]. The energy conversion efficiency (ECE) of acetate and glucose as substrates in MFC was compared at 42% with acetate but was only 3% with glucose [66].

Using complex mixtures of organic matter offers the possibility of enriching more diverse microbial communities, leading to better power generation [93].

Results in literature demonstrate that limiting substrate to the equivalent maximum current that the anode can generate, maintains MFC performance over a long term for high strength wastewaters, such as those generated in the biorefinery [92].

The substrate used to feed the lab-scale WWMFCs was acetate, considering the better performance than glucose as substrates. Generally, the solution used to fill the reactors was taken from urban waste water treatment or synthetized starting from a purified potable water, useful to isolate or controlling desiderable parameters, with the addiction of 1 g/l concentration of acetate, but other concentration values as 2 g/l was tested with similar results.

2.7 Electrodes

The materials used as anode electrodes must have several specific characteristics for improving interactions between the biofilm and the material surface. The most important characteristics are: electrical conductivity, resistance to corrosion, high mechanical strength, developed surface area, biocompatibility, environmentally friendly and low cost [108][114].

Carbonaceous- and metallic-based materials are the main types of electrode adopted, which possess all the above-mentioned characteristics [128]. Among carbonaceous materials, carbon cloth (Fig. 2.7 a), carbon brush (Fig. 2.7 b), carbon rod (Fig. 2.7 c), carbon mesh (Fig. 2.7 d), carbon veil (Fig. 2.7 e), carbon paper (Fig. 2.7 f), carbon felt (Fig. 2.7 g), granular activated carbon (Fig. 2.7 h), granular graphite(Fig. 2.7 i), carbonized cardboard (Fig. 2.7 j), graphite plate (Fig. 2.7 k) and reticulated vitreous carbon (Fig. 2.7 l) are used as commercially available materials.

Among metal-based materials, stainless steel plate (Fig. 2.7 m), stainless steel mesh (Fig. 2.7 n), stainless steel scrubber (Fig. 2.7 o), silver sheet (Fig. 2.7 p), nickel sheet (Fig. 2.7 q), copper sheet (Fig. 2.7 r), gold sheet (Fig. 2.7 s) and titanium plate (Fig. 2.7 t) are used as commercially available materials [114].
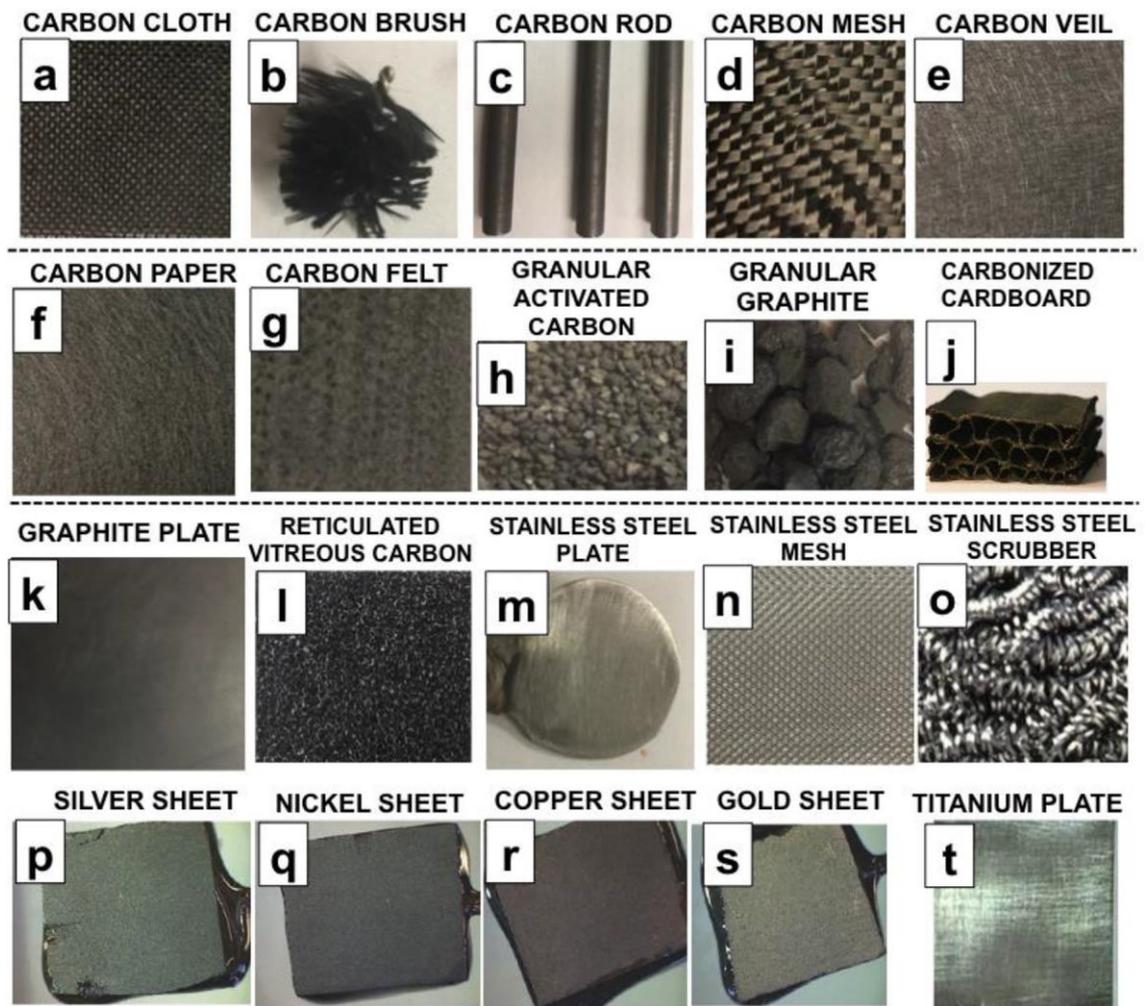
Fig. 2.7: Digital photographs of carbon cloth (a), carbon brush (b), carbon rod (c), carbon mesh (d), carbon veil (e), carbon paper (f), carbon felt (g), granular activated carbon (h), granular graphite (i), carbonized cardboard (j), graphite plate (k), reticulated vitreous carbon (l), stainless steel plate (m), stainless steel mesh (n), stainless steel scrubber (o), silver sheet (p), nickel sheet (q), copper sheet (r), gold sheet (s), titanium plate (t) (Santoro et al. [114]).

Carbon cloth is a carbonaceous material used very often as anode in MFCs [136]. This material guarantees high surface area and relatively high porosity demonstrating also high electrical conductivity, as well as flexibility and mechanical strength but the negative aspect is related to the cost that is generally quite high.

Carbon felt is a carbonaceous material that is commonly used as anode in MFC, it was used for the electrodes of lab-scale TMFCs. Its characteristics are high porosity and high electrical conductivity.

Similar to carbon veil, the large pores allow bacteria to penetrate through the structure and to build and colonize the biofilm also internally. The cost is relatively low, and the mechanical strength is high depending on the thickness of the material [120].

Carbon brush is a very interesting material based on a titanium core in which carbon fibers are twisted [74]. It was chosen as anode for WWMFCs lab-scale. The surface area is quite high with an optimal area to volume ratio. The high electrical conductivity is guaranteed by the central titanium metal that at the same time increases the material cost. Carbon brushes are heavily used as anodes and ongoing investigations are looking to bring down the overall costs [69].

2.8 Lab-scale MFC prototypes

In this paragraph, an economical way to build MFCs and the specific design lab-scale MFCs is presented. It was used two different kinds of MFC for experimentations: one is a terrestrial microbial fuel cell (TMFC) based on soil that acts as the membrane, inoculum of bacteria and as flow of nutrient, the other one is a waste water microbial fuel cell (WWMFC) where waste water acts as flow of nutrient and bacteria inoculum. Usually in an MFC reactor, the anode is placed at a working distance of about 4 cm up to 8 cm with respect to the cathode. The materials chosen for the anode and the cathode have to be electrically conductive and chemically inert, so normally the electrodes are made of graphite fiber felt and carbon cloth or brush with a diameter that varies from 8 cm to 13 cm. The structure of the reactor is usually made of PVC with cylindrical shape. All the electrical cables are made of titanium wire.

2.8.1 TMFC lab-scale

Lab-scale TMFCs (Fig. 2.8) are built from PCV with a height of 10 cm and a cylindrical shape. The reactors are filled with topsoil, preventing air bubbles inside the ground to avoid oxygen pervading into the anodic chamber. The reactor diameter measures 10 cm.
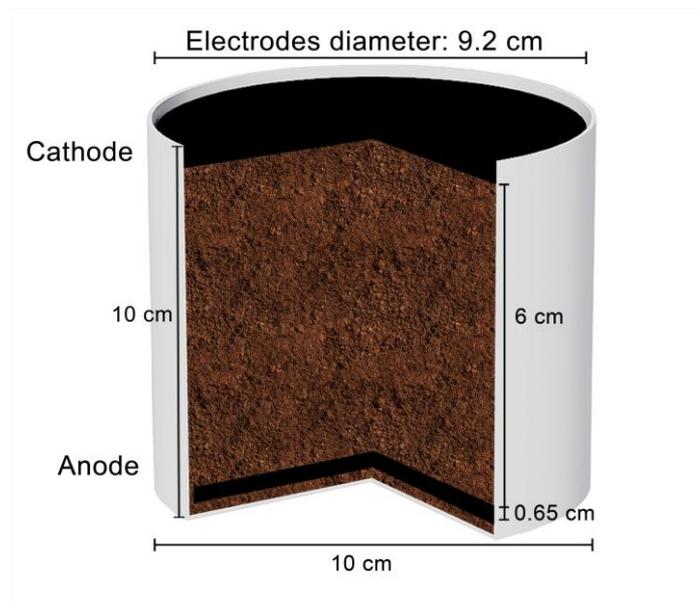
Fig. 2.8: 3D Graphical cross section of a lab-scale TMFC

The anode is placed at a working depth of about 6-8 cm into the ground, while the cathode is on top of the soil. Both electrodes were made with carbon fiber felt with a diameter of about 9.2 cm and thickness of about 0.65 cm (Fig 2.9). Fig. 2.10 shows a photo of the lab-scale TMFC.

Fig. 2.9: Photo of the electrodes used for lab-scale TMFC made of carbon felt

Fig. 2.10: Photo of a lab-scale TMFC

2.8.2 WWMFC lab-scale

WWMFCs lab-scale prototypes of cylindrical shape are made of PVC draining tube of 0.7 liters. The distance between the electrodes is about 4 cm with an anode (Fig 2.11) made with carbon fiber brush (30% Teflon treated, Fuel Cell Earth LLC, USA).

Carbon fiber brush anode

Fig. 2.11: Photo of carbon fiber brush anode

An air cathode of 120 cm^2 of carbon cloth was manually made, using a paintbrush with 1.56 mg of black carbon and 0.5 mg of platinum for every cm^2 of the cathode surface area (Fig 2.12).
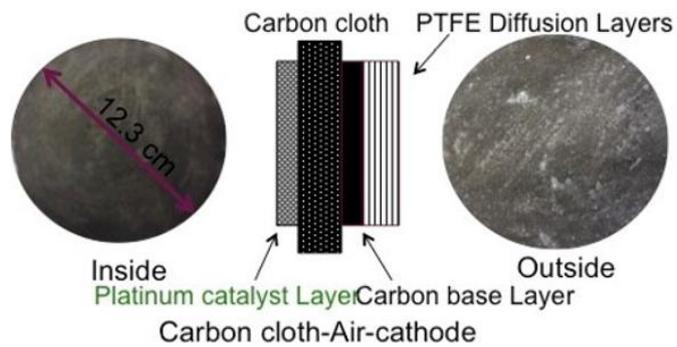
Fig. 2.12: Air cathode of lab-scale WWMFC

Figure 2.13 shows the reactor dimensions and its part size.
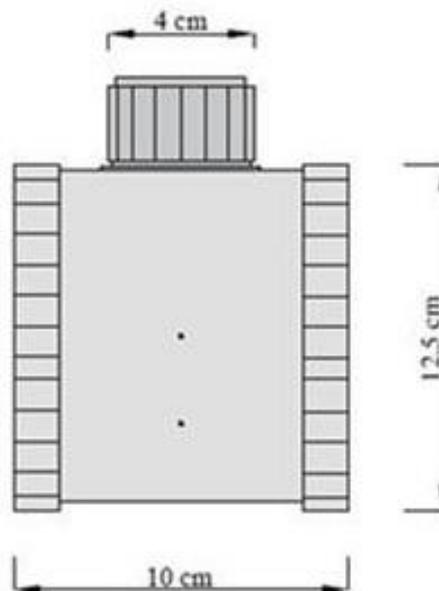
Fig. 2.13: lab-scale WWMFC dimensions

The reactors are fed with 0.7 g of sodium acetate (1g/l). WWMFCs lab-scale were operated in batch-mode and they were inoculated with urban wastewater (Limonest wastewater treatment plant, Grand Lyon, France) or synthetic waste water made with purified potable water.

Figure 2.14 shows a 3D graphical section of lab-scale WWMFC and Fig 2.15 shows a photo of the reactor.
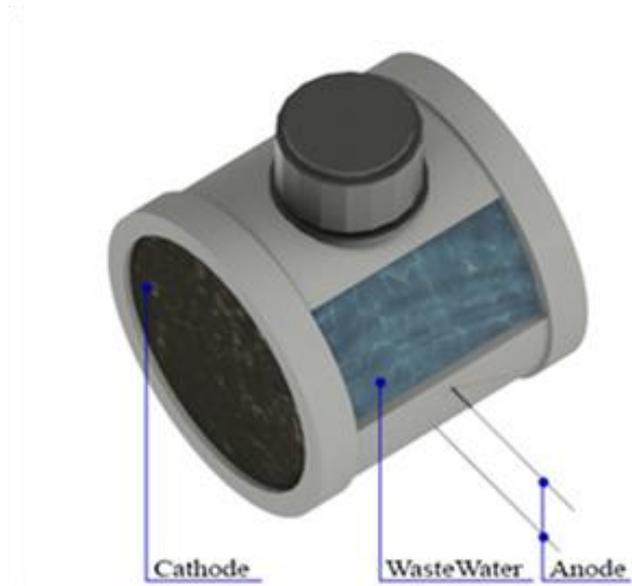
Fig. 2.14: 3D graphical section of a lab-scale WWMFC

Fig. 2.15: Photo of a lab-scale WWMFC

2.9 MFC losses and limitation

2.9.1 Energy mechanisms of an ideal MFC

Chemotrophic bacteria gain their energy for life and growth through the coupled mechanisms of nutrient oxidation and reduction (electron donation). *Chemoorganotrophs* are organisms, which oxidize the chemical bonds in *organic* compounds as their energy source. So, a chemoorganotrophs organism is one that requires organic substrates to get its carbon for growth and development, and that produces its energy from the oxidation and reduction (redox) of an organic compound.

These mechanisms involve the transformation of reactants (as organic matter and oxygen) into products (as water and carbon dioxide). Oxygen is the electron acceptor of aerobic organisms. Other inorganic compounds, such as nitrate, are the electron acceptors of anaerobic organisms.

The theoretical energy available for the bacteria is related to the difference between the energy content of the reactants and the products.

The **reaction** can be evaluated in terms of *Gibbs free energy* (G), which is a measure of the maximal work that can be derived from the overall reaction. The Gibbs free energy equation (3) represent the energy content that can be expressed as the product of the electromotive force (EMF) and the corresponding charge flow nF [2].

$$G = nF(E_{RED} - E_{OX}) \tag{3}$$

where *n* is the number of electrons involved in the reaction, F is the constant of Faraday, and E_{RED} and E_{OX} are the reduction and oxidation potentials respectively which difference corresponds to the **EMF** as in equation (4).

$$EMF = E_{RED} - E_{OX} = E_{ACCEPTOR} - E_{DONOR} = E_{cathode} - E_{anode} \tag{4}$$

So, the *electromotive force* (EMF) is the maximum potential achievable, equal to the difference between the half reactions of the electron donor and acceptor under ideal conditions.

A part of this energy, G_{BIO} is used by the microbes for growth and maintenance in the MFC as electrochemical and biological process. Therefore, the total available energy (G) of an electrochemical system significantly decreases, and the available electrical energy (G_{ELEC}) could be given by (5).

$$G_{ELEC} = G - G_{BIO} \tag{5}$$

If the biological energy (G_{BIO}) becomes too large, the output electric energy will decrease. In an MFC, bacteria transfer electrons from the substrate at a low potential to the anode. Thus, the energy gain for the bacteria is determined by the anode potential. To obtain a higher metabolic energy gain for the bacteria, a higher difference between the redox potential of the substrate and the anode potential is required.

In equation (3), the variable *n* denotes the number of electrons transferred via electron transfer mechanisms. For acetate, the maximum number of electrons transferable is 8. In a microbial metabolism, only a limited number of electrons are transferable to the anode via a certain mechanism [74][117].

Depending on the presence or absence of terminal electron acceptors, two major metabolic pathways can be distinguished: *respiration* in the presence of oxygen and *fermentation* in the absence of oxygen and exogenous oxidants.

In fermentation, electrons taken from the reduced substrates are transferred to oxidized intermediates to generate reduced fermentation products (as lactate, ethanol, hydrogen). In the presence of oxygen, fermentation is generally shut down since the energy gain through fermentation is less than with respiration of oxygen. In fact, oxygen is the electron acceptor with the highest redox potential, and as such, electrons will react with it.

Acetate is one of the most effective and common electroactive substrates. As a matter of fact, it is often used to fuel lab-scale MFCs.

When oxidized, acetate is degraded into bicarbonate according to equation (6), which is counterbalanced by equation (7).

$$(E_{anode} = 0.187V) \qquad CH_3COO^- + 4H_2O \longrightarrow 2CO_3^- + 9H^+ + 8e^- \qquad (6)$$

$$(E_{cathode} = 1.229V) \qquad 2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O \qquad (7)$$
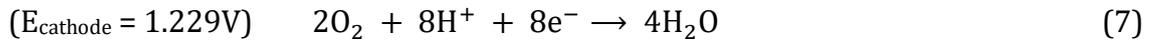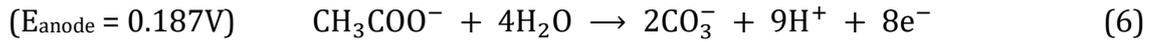
The corresponding standard potentials E_0 were determined from the Gibbs free energy data tabulated in [122] for the acetate/bicarbonate couple and in [2] for the oxygen/water couple. Therefore, the resultant EMF is 1.042V in standard conditions.

The theoretical potential of the electrode in a given typical condition can be calculated using the *Nernst equation*, that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation, as given in equation (8)

$$E = E_0 + \left(\frac{RT}{nF}\right) \ln \beta \qquad (8)$$

where E_0 is the standard cell potential (free energy at 298 K, 1 bar, 1 Mol, reported versus standard hydrogen electrode), R is the ideal gas constant (8.314 J/Kmol), T is the temperature (K), F is the Faraday constant, *n* is the number of moles of electrons transferred and β is the reaction quotient which is the ratio between the chemical activity of the reduced form and the chemical activity of the oxidized form.

The Nernst Equation is derived from the Gibbs free energy under standard conditions associated with an electrochemical transformation. The theoretical redox potential value of the anode and the cathode are 0.187 V and 1.229 V respectively at standard conditions (298 K, [H+] =1 M) as in (6) e (7).

In [76] the theoretical anode and cathode potentials under specific conditions in a microbial fuel cell was calculated, with an acetate oxidizing anode ($HCO3^-$ = 5 mM, CH3COO$^-$ = 5 mM, pH = 7) and an oxygen reducing cathode (partial pressure pO2 = 0:2, pH = 7) and shown to have the theoretical anode potential of –0.296 V and the

theoretical cathode potential of 0.805. Accordingly, the EMF is 0.805-(-0.296) = 1.101V.

So, the maximum voltage difference reachable with MFC, which uses the acetate as substrate and the oxygen as electron acceptor is equal to EMF = 1.101 V. Anyway, the maximum theoretical value can't be achieved in practice due to various possible losses in term of current and voltage.

2.9.2 Voltage losses

In bioelectrochemical systems, voltage losses can be divided into bacterial metabolic losses, ohmic and electrode over-potentials losses of the system.

- **Activation losses**: as described in the previous section bacteria capture a fraction of the energy content of the substrate for their growth and maintenance and it causes in part a voltage losses. The voltage losses V_{BAC} have to be deduced from the EMF. Considering that bacteria activate the reaction at the anode, the voltage drop V_{BAC} can be included in the more general definition of *activation losses* that also includes phenomena at the cathode. A proportion of the voltage generated is lost in the beginning of chemical reactions that transfer electrons to or from the electrode. It results from the large local potential difference necessary to allow a reaction at the electrodes. The dynamics of phenomenon are diverse and are related to the storage of energy by bacteria, metabolic shifts, and evolution of the microbial community. Activation losses occur in abiotic conditions and in chemical fuel cells since these are related to overcoming the initial energy barriers that are involved at the start of chemical reactions. This voltage drop is highly *non-linear*. The activation voltage losses are one of the most relevant causes of voltage drop. An increase of the electrode surface area can lower the activation resistance. Moreover, a raise of operative temperature can reduce activation losses.

- **Ohmic losses** is caused by resistance in interconnections and in the electrolyte. This drop has a fast dynamic with an *instant* change of the output current. The ohmic voltage losses is the linear resistance to the flow of electrons through the material of the electrodes and the various interconnections, as well as the

resistance to the flow of ions through the electrolyte. This voltage drop is essentially proportional to current density following Ohm's low. Ohmic limitation is mostly due to the resistance of electrolytes and the various interconnections. The ohmic resistance can be reduced by optimizing the distance between the electrodes, increasing solution conductivity and by checking thoroughly all electric contacts.

- **Concentration losses** or mass transport losses is a resistance caused by the delayed diffusion of reactants and products to the reaction site and out of it. Also, it is caused by the change in concentration of the reactants at the surface of the electrodes, where the substrate is used as fuel. Concentration drops are amplified for high current densities, when the reactants are consumed at high rates at the surface of the electrodes. So, it is possible to limit the effect of the concentration losses by controlling current density.

Local concentrations directly affect the electrode potentials according to the *Nernst Equation* (9) [2].

$$E = E_0 + \left(\frac{RT}{nF}\right) \ln \frac{(reactants)}{(products)} \tag{9}$$

For each electron involved in the redox reactions, the total theoretical energy available is shared between the bacteria, the electrical load and the losses.

The unit that represents the voltage losses is the *Potential Efficiency* (PE). It decreases at high current densities.

PE is defined in (10) as the fraction of the actual output voltage versus the theoretical potential of the involved reaction.

$$PE = \frac{Vout}{E_{red} - E_{ox}} \tag{10}$$

considering V_{OUT} as the MFC output voltage.

The potential efficiency may vary with respect to different designs and operating conditions. Very low values of PE of 2-6% were reported with glucose, whereas better performance was reported with acetate for a resulting PE of 26–59% [85].

2.9.3 Current losses

In an ideal MFC, the anode is the unique ultimate electron acceptor available to bacteria for the oxidation of the substrate.

In practice however, a fraction of electrons may well migrate to the cathode through the electrolyte or react with alternative electron acceptors like oxygen and non-organic oxidants.

It can happen due to eventually the presence of oxygen diffusing in the anodic compartment, in particular when some air bubbles remain inside the soil in TMFC. Another reason can be the naturally present in the substrate of non-organic electron-accepting molecules as *nitrate* and *sulfate* [61][133], especially when the substrate is wastewater.

Finally, in the absence of viable electron acceptor, some bacteria are able to develop fermentative metabolic pathways, in place of respiration pathways.

When the MFC is in short-circuit condition, the potential of the anode is close to the potential at the cathode, and the anode is therefore strongly attractive. Bacteria will mostly use the anode as an electron acceptor. Other comparatively strong alternative electron acceptors such as diffused oxygen will divert electrons.

When the MFC is in open-circuit condition, the anode does not attract any electrons, and bacteria are more likely to select alternative electron acceptors, in the order of diffused oxygen, non-organic acceptors, and eventually also fermentation.

As a matter of facts, the higher the output voltage V_{OUT}, the less attractive the anode, and the more electrons to be quenched by competitive electron acceptors. [29].

The *Coulombic Efficiency* (CE) is a unit representative of electron losses within MFC as defined by (11).

$$CE = \frac{n_{eff}}{n_{total}} \tag{11}$$

It represents the percentage of electrons recovered from the organic matter (n_{eff}) versus the theoretical maximum number of electrons (n_{tot}) involved in the oxidation reaction.

The unit representative of current losses is the Coulombic Efficiency (CE) that could also be defined as in (12). It is the fraction of electrons effectively used as current versus the total number of electrons n (mol) involved in the internal reactions.

$$CE = \frac{Q_{effective}}{Q_{total}} = \frac{\int IdT}{n \times F} \tag{12}$$

where $Q_{effective}$ corresponds to the amount of charge transferred to the anode and Q_{total} corresponds to the total amount of charge produced by the oxidation reaction. The term I is the output current. The electrons that are not transferred to the anode are called "quenched electrons" and can be represented as a current I_Q.

2.9.4   Load influence

In an ideal microbial fuel cell, the potential difference between the fuel and the terminal electron acceptor is shared between the bacteria and the outer electrical load. The potential difference available for the bacteria corresponds to the one between the anode and the fuel. The potential difference available for the outer electrical load corresponds to the one between the cathode and the anode.

The output voltage and energy conversion efficiency are functions of the given output load of the MFC. This suggests that the efficiency of the MFC is optimal for a given external load value. The output load, therefore, should be, adjusted in order

to maximize the efficiency. The output voltage of the MFC increases with the load. When the load reaches high values, the output voltage begins to saturate. The output voltage and efficiency are affected in a different way as shown in Fig 2.16 and Fig. 2.17 respectively. The set up was a WWMFC lab-scale fed by real urban waste water.
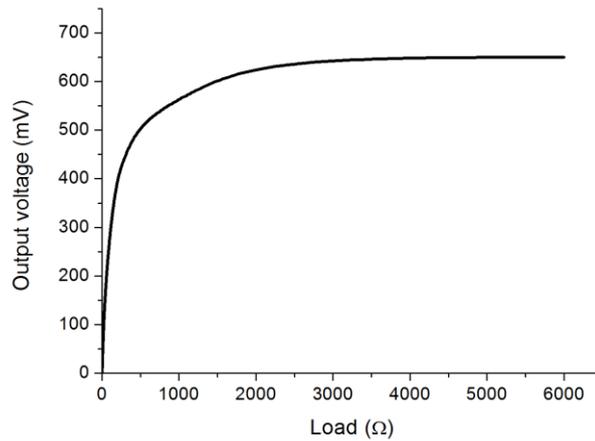

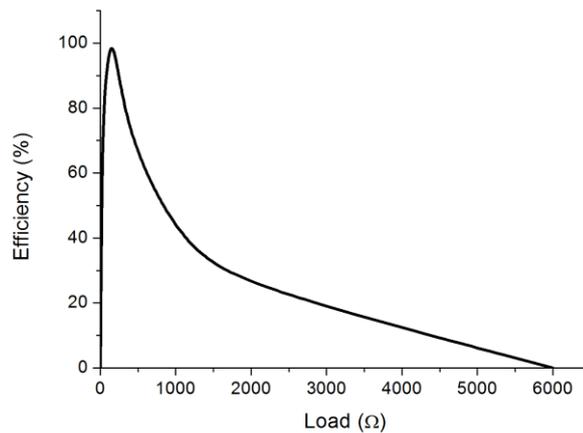Fig. 2.16: Typical effect of load on MFC output voltage[29]

Fig. 2.17: Typical effect of load on MFC efficiency[29]

The voltage losses during the different operations of an MFC are schematically shown in Fig. 2.18. The corresponding drops are plotted for different load scenarios ranging from open-circuit to short-circuit. The sub-plot at the right-

bottom corner represents the proportion of electrons transferred to the anode or diverted in alternative electron acceptors [29].
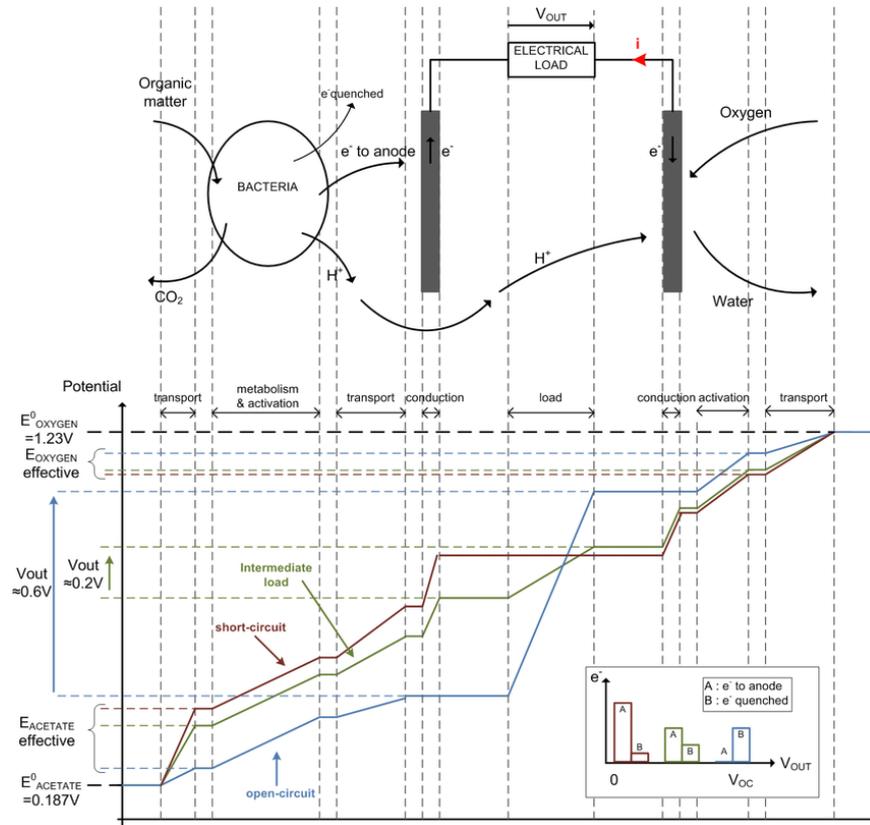
Fig. 2.18: Qualitative graph of the voltage drop in the different parts of MFC when electrical load is applied [29]

2.9.5 Internal resistance

The internal resistance of a cell is dependent on its size, chemical properties, age, temperature, and the discharge current. The constructive parameters of a cell define its internal resistance value.

The electrochemical limitations on the performance of microbial fuel cells (MFCs) are due to the internal resistance (R_{int}), which is caused by different mechanisms including ohmic, activation, and mass transport losses.

As a matter of fact, the open circuit voltage measured is lower than the theoretical value although there is no current through the MFC. When a load is connected to the MFC, a current start to flow in the circuit.

The output voltage decreases due to the losses in the R_{int}. The internal resistance is a critical factor to determine the output voltage of MFC. A wide literature concerns the minimization of R_{int} relying on its structural and operational affecting parameters [64].

Ohmic, activation and concentration resistance affecting the internal load of MFC.

The output voltage and energy conversion efficiency are functions of the given output load of the MFC. The **Maximum Power Point** (MPP) value can be find under *impedance matching* condition to maximize the output power, so the output load needs to be given at the same value of the internal resistance.

Also, for a multiple connection of MFCs, the impedance matching of MFCs is crucial to avoid losses. Ideally, the maximum power transfer for MFCs in connection, the MFCs need to have the same internal load value.

The efficiency of MFCs is optimal for a given external load value that match the internal load value. The output load, therefore, should be, adjusted in order to maximize the efficiency. It usually requires a maximum power point tracking (MPPT) algorithm to find the best impedance matching.

Also, another important parameter is the fact that MFC can operate both during biofilm maturation and when the biofilm is mature. The electrical operating point is interlinked with the metabolism of bacteria and to other internal mechanisms such as mass transport phenomena and as such it influences the short-term and long-term production of electrical energy and consumption of organic matter.

Reduction the value of the R_{int} can increase the maximum currents observed during polarization because it decreases the phenomena associated with mass transfer or kinetic limitations. In the removal rate was investigated for different output resistances [29].

Also, as was observed in [58] for high resistance values (low current densities) the chemical oxygen demand (COD) is reduced more slowly. The COD removal rates are indicators of how fast the organic matter is consumed. It is directly linked to the reaction rate and as such to the output current. In addition, at high resistance value, a difference in bacterial metabolism is observed with an increase in the production of short chain fatty acids [110].

2.10 Main measurement and electrical issues

The electrical behaviour of an MFC is influenced from many factors, some relate the single reactor performance and other concerning multiple reactors that are connected together.

Many parameters such as pH value of soil in TMFCs and of the solution in WWMFCs, the temperature, the substrate concentration, the biofilm regeneration, the bacteria metabolism and population grown must be taken into account and checked.

2.10.1 Reducing internal load and MFC limitations

Reducing the internal resistance is also crucial for single reactor electrical performance.

The *Ohmic resistance* can be reduced by checking carefully all contacts and increasing solution conductivity. Activation resistance can be reduced by increasing the electrode surface area and increasing the operating temperature until it is tolerated by the bacteria. The effect of the concentration resistance can be limited by control of the current density. [29]

Increasing available electrons on the electrodes by imposing a voltage from an external source on the cathode seems to improve the current production and electrical performance probably due to a reduction on activation losses. This polarization process can be done by imposing an external voltage to the cathode, because this leads the cell to be instantly charged to the imposed voltage.

2.10.2 Large stack of MFCs: issues and impedance mismatching

When MFCs are more than one, different connections are conceivable: serial or parallel connection, or a combination of both (series/parallel).

The parallel connection usually can increase currents and is similar to scaling-up MFC in volume, voltage value tends to the mean of voltage value of cells. The series connection instead provides an increase in the resultant voltage, but currents can be easily affected from cable resistance of long wires and imperfect connections.

Also, design parameters of reactors are important. Non-uniformity in manufacturing process of reactors can result in an *impedance mismatch* among cells. Whether it is caused by fuel supply, microbial or reactor non-uniformities, the impedance mismatch is the reason for voltage reversal.

Voltage reversal is detrimental to power generation because the concerned MFC absorbs the energy produced from the others.

2.10.3 Avoid oxygen presence in the anodic chamber

It is appropriate to prevent the presence of oxygen in the anodic compartment, to avoid it to react as alternative electron acceptors instead of the electrode.

Usually non-organic electron-accepting molecules as *nitrate* and *sulfate* are naturally present in the substrate in waste water. An artificial waste water was properly synthetized from purified potable water to avoid their presence for experimentations on lab-scale WWMFCs. The presence of non-organic electron acceptor molecules can be avoided if previously a depollution is carried out to waste water, before fuelling the reactors.

Considering terrestrial microbial fuel cell is important to keep away the presence of *air bubbles* within the soil present in the anodic chamber.

2.10.4 Maximum power point tracking (MPPT)

In any energy harvesting system from low-power transducers (photovoltaic, thermoelectric generators, fuel cells, etc.), the system should be able to extract as much energy as possible from the source.

So, power management systems must operate at their maximum power point (MPP). MPP varies with the operating conditions. An example is the operation of photovoltaic that varies with insolation, temperature and other effects.

On the power curve of the source (power–voltage), there is only one point between the open circuit and the short circuit, called maximum power point (MPP) where power is maximum.

A power DC/DC (buck/boost/buck– boost/flyback) converter is usually used also to achieve the MPPT, placed between the source and the load. Fig 2.19 shows a block diagram of a MPPT controller for energy harvesting systems. These systems use complex algorithms to ensure that the transducer always operates at its MPP. These algorithms are called maximum power point techniques (MPPTs). A digital controller is generally used to control the converter. A number of MPPT methods have been reported in literature [89, 125] and some commercial DC/DC converters include one, e.g. as the BQ25504 converter.
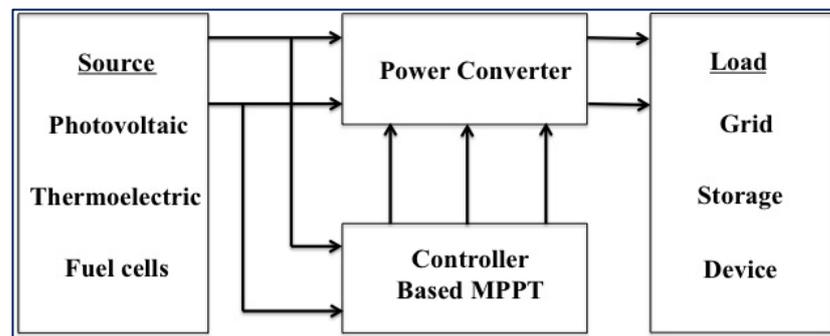

Fig. 2.19: MPPT controller for energy harvesting systems block scheme

3. MEASURING BOARD

3.1 Introduction

An original measuring board dedicated to the electrical characterization of MFC was developed to allow automatic and self-managed long-time tests (Fig. 3.1). Performing an electrical characterization enables to understand the dynamics of the cell and its electrical performance. It is possible to find many parameters related to the cell as the internal resistance values and so the maximum power point, the voltage, current and power values in every desired boundary conditions.

Moreover, it enables to reproduce long-time experiments in automation and can be useful to understand the sensitivity of major parameters on MFC behaviour during the charge and discharge phase or using a wide collection of loads, collecting easily the steady-state, pseudo steady-state and real time values.
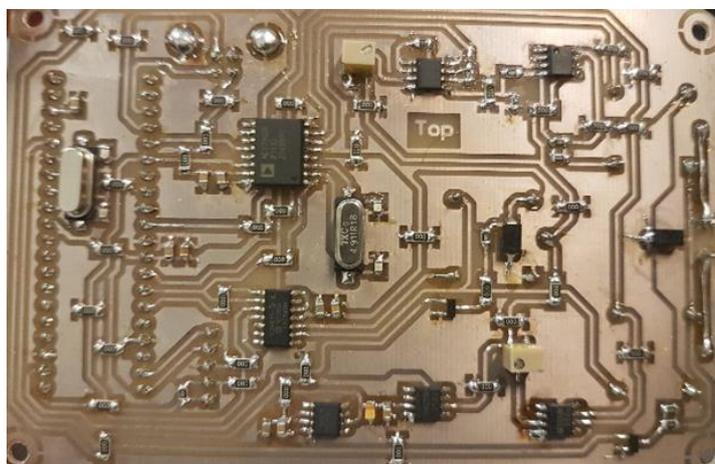

Fig. 3.1: Photo of the top layer of the Measuring Board

3.2 Design of a measuring instrument dedicated to MFC

3.2.1 Power supply and accurate voltage reference

The custom measuring board is supplied by a +5 V_{cc} provided through **USB port** that must be connected to a computer. The USB port can provide a 5 V supply on a single wire to power connected USB devices. A device may draw usually a maximum of 500 mA from a USB 2.0.

A voltage reference "**REF192** Series" by Analog Device is used to obtain an accurate reference voltage of 2.5V exploited by the circuit for the comparison of the input data.

Rail-to-rail operational amplifier "**TS921**" is used as buffer amplifier to maintain an accurate value of reference voltage by supplying the necessary current to the circuit.

In the case of a load coupled directly, as the demand for current from the load increases, the reference voltage changes showing a REF192's load regulation of some units of ppm/mA. Therefore, the "TS921" acts as a current buffer to prevent REF192 directly supply the current to the load. "TS921" avoids an inappropriate "REF192" bias point.

3.2.2 Measurement phase selector (Charge, Discharge, Power analysis)

Three electromagnetic relays "LEG-5" by RAYEX ELEC permit to switch between the three options for the measurement:

1) a *discharge phase* by imposing zero voltage value to the reactor (V=0 V, R=0 Ω, short-circuit), measuring current intensity.

2) a *charge phase* by imposing zero current intensity value to the cell (I=0 A, R=∞, open-circuit), measuring voltage.

3) a *power analysis phase*, operating as *resistorstat* by switching load values. It can be considered as a case of discharge phase but with a varying load value applied and both current and voltage measurement.

The three relays are managed by the user choosing between the options of the graphical unit interface (GUI).

Among the features of the GUI there is the possibility to switch the on-going measurement phase, the user command is sent to the microcontroller that switches the proper relay. A schematic of the board is provided in Fig. 3.3.

In the schematic of the system in Fig. 3.4 shows the main operation of the measuring system.

The Relay **2** is placed between the positive input of the cell and, in case of switch ON, to the negative input of the "LMP7721" and the transimpedance block or, in case of switch OFF, to the analog input of the "AD7706" .

The Relay **3** is placed between the negative input of the cell and in case of switch OFF, to the "AD7706" and the negative pole of the voltage reference or in case of switch ON to the Relay **1**.

When the *charge phase* is selected from the features of the GUI, both the Relays **2** and **3** will give the connection lines to the "ADC AD7706" for differential comparison of the input voltage (Fig. 3.5). When in *discharge phase,* the Relay **3** enables the connection line to the negative pole of the 2.5V reference and the Relay **2** enables the connection line to the transimpedance block, composed of the "LMP7721" and the "TS912", to measure the current that is flowing out of the MFC (Fig. 3.6).

The Relay **1** has the role of enabling the *power analysis phase* (Fig. 3.7), where the measurement instrument works also as an automatic *resistorstat*. It is placed between the "MCP4241", 10k Digital potentiometer, the Relay **3** and the positive input of a precision operational amplifier "LMP7721" used to compare the input values. The Relay **1** is piloted by the Relay **3**. In fact, only if the Relay **3** is switched on to perform voltage measurement, the Relay **1** can function properly.

When the Relay **1** is switched on, the pin 3 will be connected to the pin 2 (case switch ON), it allows the operation of the digital potentiometer "MCP4241". It can switch the resistance values applied as load to the input. In this way it is possible to perform the power analysis of the cell by measuring voltage and current corresponding to each load value and find the maximum power point (MPP).

When the Relay **1** is switched off, the pin 3 will be connected to the pin 5 (case switch OFF) the "MCP4241" is bypassed so the phase turns into a normal dis*charge phase* with zero load to enable the cell to be discharged.

In the following *switching table* are described the different relays position in base of the current measurement configuration.

Relays	Voltage measurement	Current Measurement	Power Measurement
RELAY 1	OFF	OFF	ON
RELAY 2	ON	OFF	OFF
RELAY 3	OFF	ON	ON

Table 3.1: Switching table explain the relays position in base of current measurement configuration
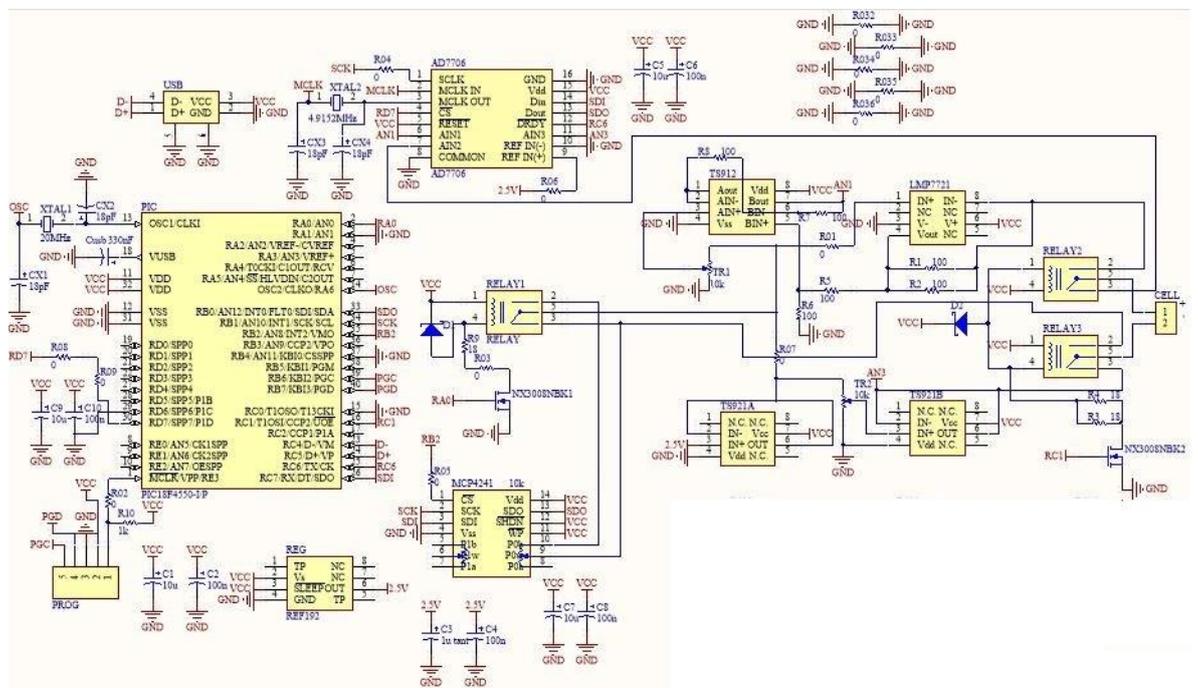

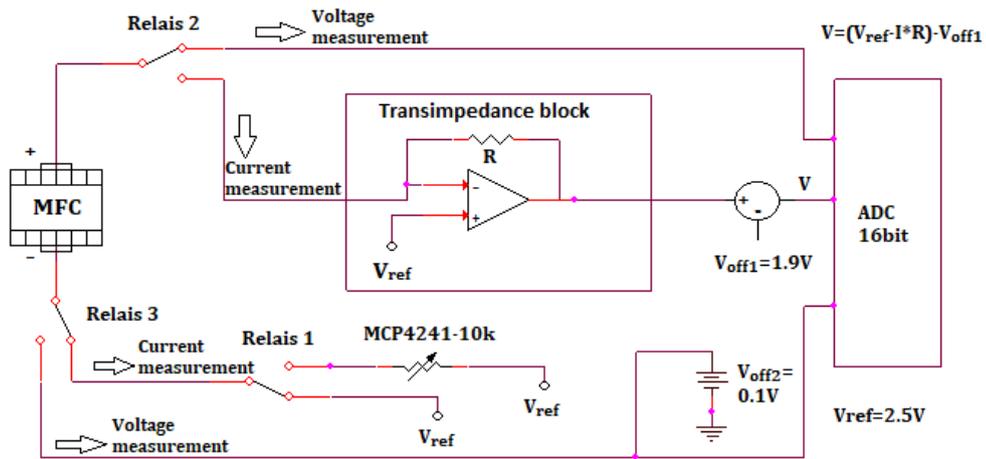*Fig. 3.3: Schematics of the custom measuring instrument*

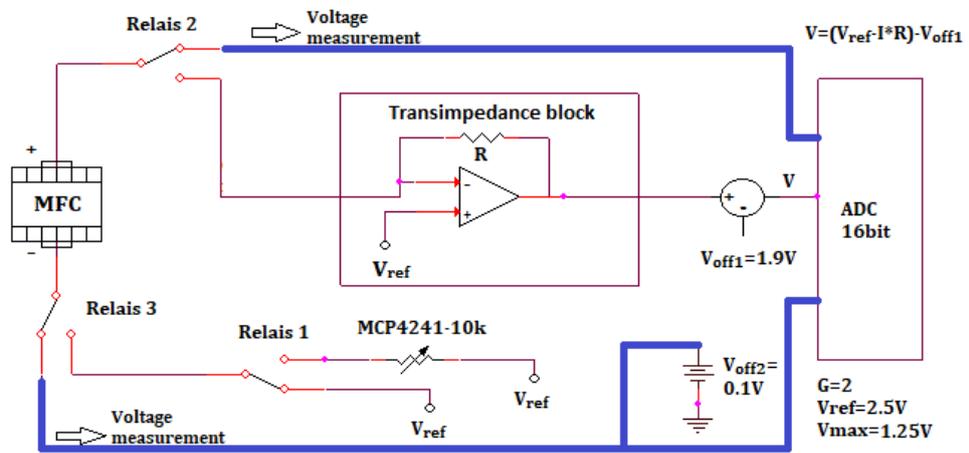*Fig. 3.4: Block Diagram of the custom measuring instrument*

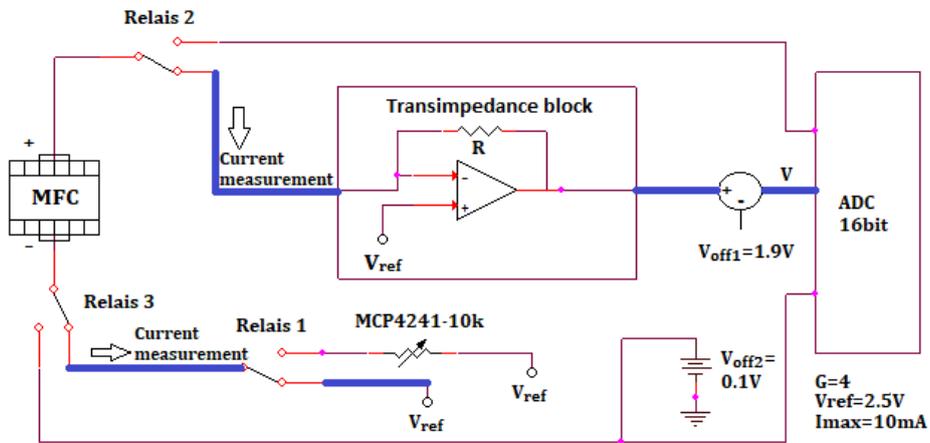*Fig. 3.5: Voltage measurement Block Diagram*

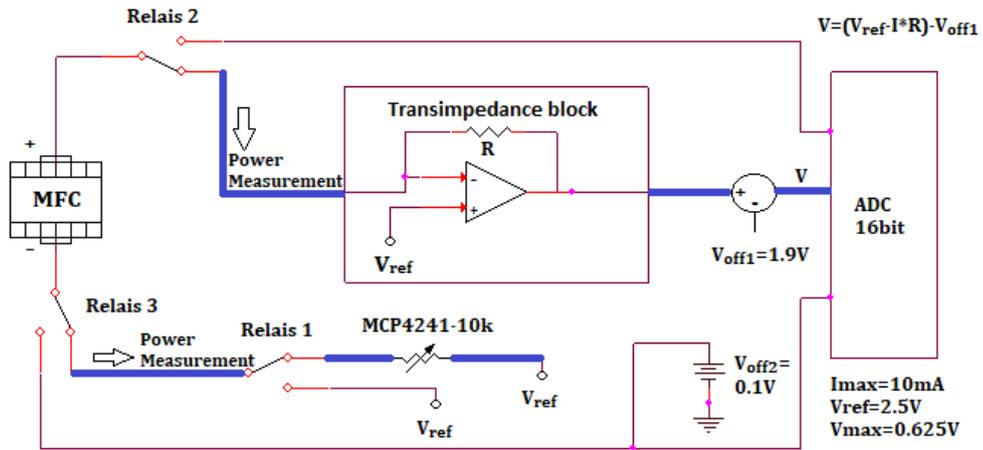*Fig. 3.6: Current measurement Block Diagram*

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Fig. 3.7: Power measurement Block Diagram

3.2.3 Current and voltage measurements

A reference voltage of 2.5V is an input to the "ADC AD7706" from the "REF192"; the ADC has three lines that were used for the input.

Two input lines were used for the **voltage measurement** (Fig 3.5)with a value of *gain* of the ADC set to 2. The resolution of voltage measurement is 18 μV and the maximum readable voltage is 1.15 V, considering that the max value is **V_{max} =1.25 V** but over V_{off2}=0.1 V

One input line was used for the **current measurement** (Fig 3.6) with a value of *gain* set to 4. It was chosen 4 as gain value instead of 2 to maintain adequate precision in the measurement. In this way the maximum readable current is 10 mA with enough resolution on current measurement of 0.2 μA.

As shown in Fig. 3.8 the equation represented at the input of "AD7706" from the adder element is:

$$V = \left(V_{ref} - I * R\right) - V_{off1}$$

The max possible voltage readable from the ADC is $V_{maxReadable}$=0.625 V, but the voltage value at the input of the ADC can be Vmax=0.6 V, considering that V_{ref}=2.5 V, V_{off1}=1.9 V and R=50 Ω.

60

The **readable range** of voltage values from the ADC is from V=0.1 V to V=0.625 V, in correspondence with a current intensity measurement of I=I$_{max}$ and I=0 A flowing in the transimpedance block.

It is possible to consider a maximum current of I$_{max}$= 10 mA before system saturation (could be up to 12 mA for 0,625 V/50 Ω).

3.2.4 Offset voltage, amplifier and transimpedance block

A precision operational amplifier **LMP7721** with ultra-low input bias current of 3 fA is used to compare the input values. The package used was SOIC8. The voltage supply range is from 1.8 V and 5.5 V. The supply current needed is 1.3 mA.

The LMP7721 is active in the discharge phase to perform current measurements, and it has been used as transimpedance.

The **transimpedance block** (Fig. 3.8) has an output that follows equation:

$$V_{out} = I * R$$

with R=50 Ω, this value was used in the circuit.

The possible values of V$_{out}$ are:

$$V_{out} = 0.5\,V = 10\,mA * 50\,\Omega$$

when I=10 mA=I$_{max}$,

or:

$$V_{out} = 0\,V$$

when I=0 mA.
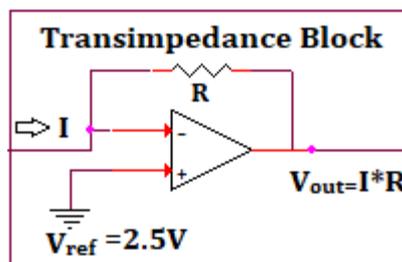
Fig. 3.8: Transimpedance block schematic

Moreover, **TS912** device, a rail-to-rail CMOS dual operational amplifier is used to build the amplifier block. Channel A acts as a negative reference and the channel B acts as an adder between current and offset voltage of V_{off1}=1.9 V.

Two 3224W-1-103E **Trimmer** Resistors 10 kΩ (TR1 and TR2, Bourns) were put inside the circuit to obtain an offset voltage value of 1.9 V from the reference voltage of 2.5V provided from REF192. The trimmer is a 4 mm SMD Trimming Potentiometer.

3.3 Instrument advantages and GUI features

One original advantage is the sensitivity of the *resistorstat,* and it can automatically switch load value after the measured value is stabilized. It means that the last measured value is checked if in respect to the precedent one (desired delta value), this can be set by the feature of the graphical unit interface (GUI). That feature allows to collect the best correct measurements avoiding wasting time or collecting useless measurements. The GUI (Fig. 3.9) was developed in C++ code.
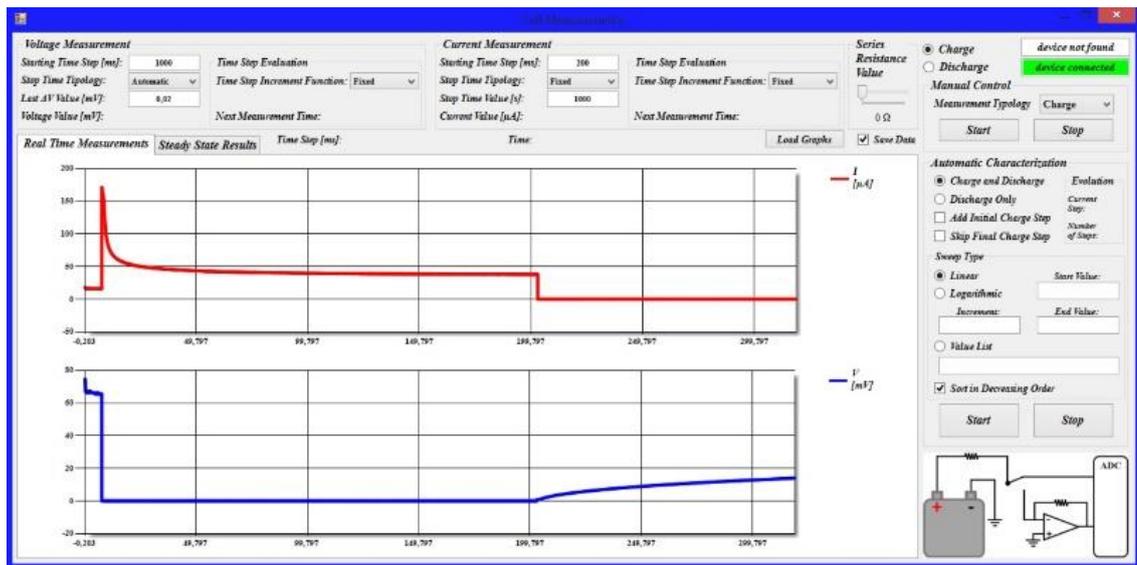
Fig. 3.9: Graphical user interface (GUI) to manage the measurements

Another important feature is the possibility to choose for the power analysis phase to alternate a phase of charge after each discharge phase with a certain load to return the voltage value to the OCV value before switch to the next load.

The range of the **dynamics** of the measurement is optimized with respect to the MFC electrical behaviour. The *current range* is from 0 to 10 mA.

Instead, the *voltage range* is from 0 to 1.15 V, considering the theoretical maximum value reached from an MFC is not more than 1.2 V, the device is able to test any kind of microbial fuel cell. Moreover, it is possible to perform test a stack of many MFCs in parallel connection and some cells in series connection (max voltage 1.15 V).

Considering the range in current and voltage, it is possible to characterize microbial fuel cell as a single reactor or in parallel connection for a stack of reactors or in series configuration up to two or three reactors.

The board resolution is high. In particular, for current intensity measurement the resolution is 0.2 μA and regarding voltage is about 18 μV, considering a 16-bit ADC.

Performing tests with different configurations and setup leads to improving the comprehension of the influence of the main parameters on the cell electrical behaviour.

All data and graphs were automatically saved after the end of each measurement.

A WWMFC can be fed with synthetic wastewater to isolate parameters or controlling their desired values to perform full electrical characterization tests using the measuring instrument to collect and store results.

The custom instrument board dedicated to the electrical characterization of the MFC can analyse electrical parameters as instantaneous power, open circuit voltage, instant current, internal resistance and electric charge. Electric charge is the measurement of capacitance behaviour of the cell.

4. I-V EXPERIMENTAL RESULTS

4.1 TMFC

The electrical performance of TMFC was examined focusing to achieve best value of power generation and the possibility to use as a biosensor. Acting on several parameters as type of soil, pH, temperature, water content and type of bacteria, it was reached best value for lab-scale TMFC. Figure 4.1 and 4.2 show the results with the best power generation and OCV value generated by lab-scale TMFC, for which different configurations have been tested. A clay soil was used with a pH value of 6.3 for the first sample (Test A) and a peaty soil for the second sample with a pH value of 7.2 (Test B). It was obtained best values of voltage with test B, of about 660 mV with the sample characterized by a value of pH = 7.2 and temperature value of 28°C and no external bacteria inoculation, the soil acts as source of microorganisms

The maximum production of power, with a load resistance of 1000 ohms, is equal to 0.31 mW, corresponding to a current level of around 0.5 mA. A power density of 46.58 mW/m^2 has been obtained.
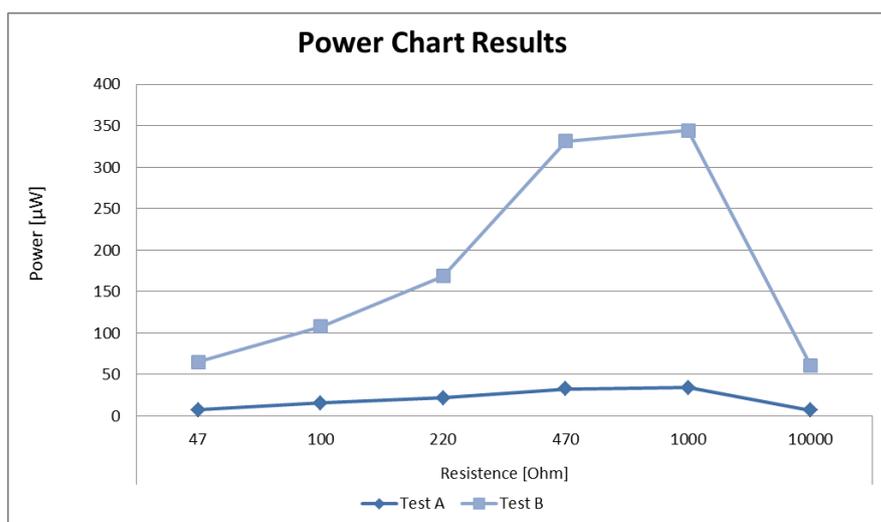
Figure 4.1. Chart results of power generation achieved by 2 TMFCs

The maximum power point MPP was found with an *external load* of 1 kΩ: it does mean that the *internal resistance* was of the same value. The terrestrial microbial fuel cell suffers from a higher internal resistance value with respect to other WWMFC due to the presence of soil instead of a liquid substrate.
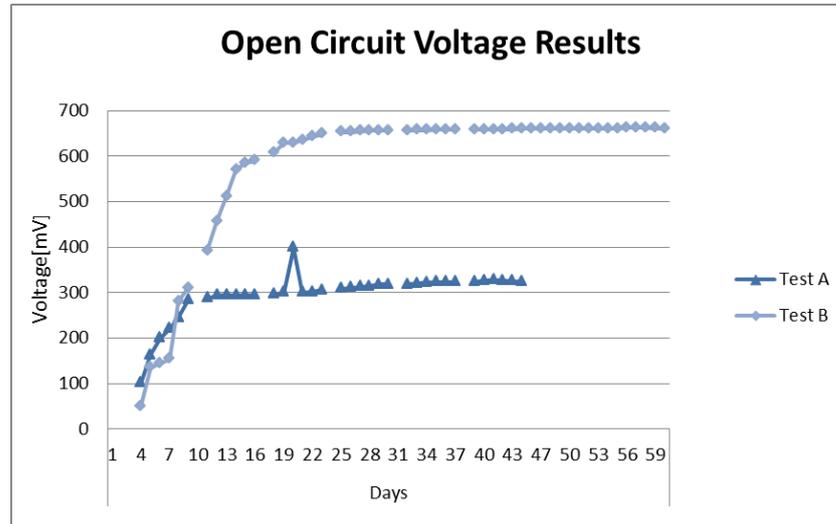
Fig. 4.2: OCV chart results of 2 TMFCs

The presence of **bacteria on electrodes** was observed and analysed to evaluate any benefits, in terms of energy yield, related to the occurrence of a single bacterial strain acting inside the MFCs. TMFCs were tested to establish which were the most present and active bacterial species within the MFCs made.

In this regard, electrode samples were taken from an active TMFC, through sterilized metal tongs, ten days after the start of the experiment, a time interval sufficient for the formation of the bacterial colony and a biofilm around the anode. The electrode samples were analysed with a microscope. A photo of the gram-negative bacteria was obtained with microscope before and after a process for isolation of the *Pseudomonas* bacterial strain (Fig. 4.3).
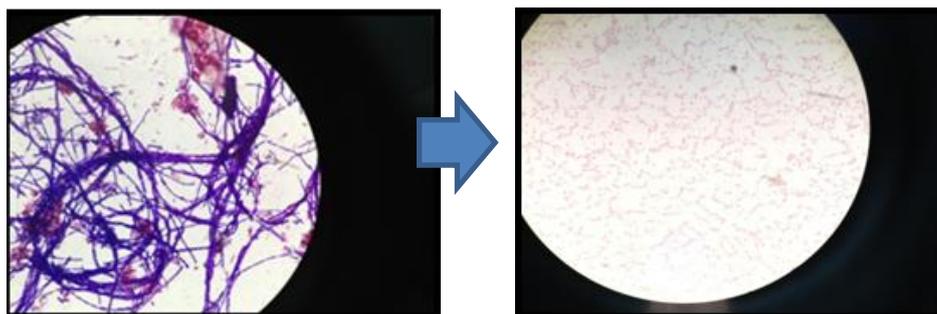
Fig. 4.3: photo with microscope of bacteria before and after isolation process of the Pseudomonas bacterial strain.

The isolated species was then stored in a nutrient agar awaiting the results from the PCR (Polymerase chain reaction) analysis, necessary to confirm the presence of the identified bacteria.

PCR analysis is a DNA amplification technique that allows to obtain "molecular fingerprinting", that is a sort of digital molecular mark that allows to distinguish a given microorganism from "individuals" related from the genetic point of view.

The analysis PCR confirmed the presence of **Pseudomonas bacteria family** on the TMFC electrode and that it was the most popular bacteria.

4.1.1 Influence of pH

The voltage generated by MFC can be exploited to analyze some parameters, particularly the pH value, allowing environmental monitoring through a sensor without environmental impact.

MFC performance depends on the pH because it causes alterations in concentration of ions, biofilm formation, membrane potential and proton-motive force. It was performed a series of test to study the usability of a TMFC also as a pH biosensor.

For a new experimentation, it was set up four reactors under different conditions to perform the test of pH dependence.

In the first one, specimen A, was used a soil from bean cultivation, with pH value of 6.29, which we measured with a pH meter [121]. Second reactor, specimen B, was prepared with soil taken from a jasmine plant with pH value of 6.8.

The third and fourth reactors, specimens C and D, were prepared with the same type of soil, used for agricultural purposes and taken from Abruzzi Region, with a pH value of 6, but in the fourth reactor 5 mL of a phosphate buffer solution, pH =7.5 (10 mM) was added, what brought the soil pH value of specimen D to increase to 6.63 [121].

In this way we monitored the influence of pH on the output voltage, in the case of reactors with different soils at diverse pH values and in the case of two reactors containing the same soil type separate pH values. The open circuit voltage (OCV) of all reactors were tested every day for a period of 10 days.

Experimental results in Fig. 4.4 clearly show that a higher pH value determines a higher voltage production both in the case of reactors with different soil at diverse pH values and in the case of reactors with same soil but different pH values.

The figure 4.4 shows how the specimen D produces a higher voltage compared to the specimen C even if the soil and the condition was the same apart from the pH value. The reactor is therefore influenced by different values of pH which increases the voltage in case of a higher pH value.
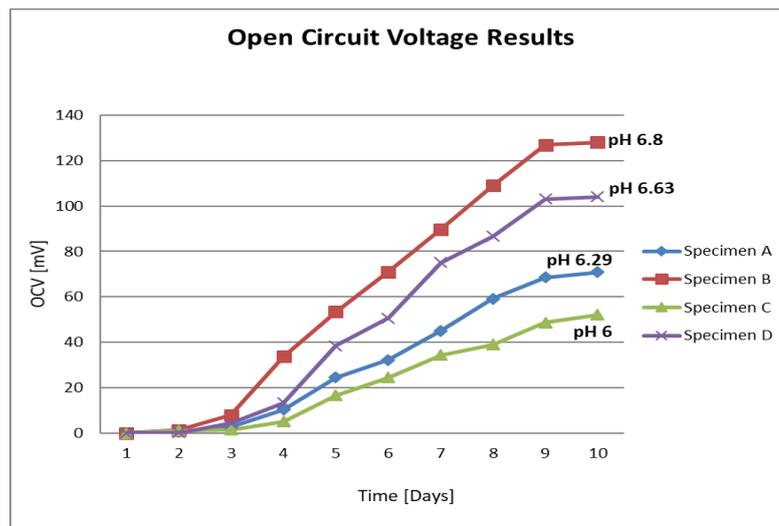

Fig 4.4: Open Circuit Potential evolution chart results.

This is due to the fact that optimal growth of bacteria requires a pH close to value between 6 and 9 [42]. As a matter of fact, an environment with neutral pH value is the best condition for the proliferation of microorganisms: this is the reason that explains the improving of the voltage level produced by TMFC reactor.

4.2 WWMFC

4.2.1 Synthetic wastewater

A *synthetic* waste water was made to feed the reactors starting from purified potable water in the labs of chemical engineering of Sapienza University. Considering that only bacteria and organic matter are present, the reactors should have minor performance in place of a real urban waste water. Anyway, the synthetic waste water created in lab contain only what is desirable and controlled. The pH value of the water can be imposed as other parameters.

The pH value of the synthetic waste water was imposed at 7.2: this value was the same of that of the waste water taken from the urban waste water treatment in Lyon. The waste water used for some experiment in Lyon was analysed in chemical engineering labs at Sapienza University.

The resulting value of the test made on the real waste water was 7.2 pH, so the value of a common real urban waste water was near to the neutral value, the best for the environment of bacteria.

The test on the real urban waste water provided the total organic carbon value (TOC). Figure 4.5 shows the results of the test on real waste water. The test was performed on the waste water after three months it was taken from Lyon urban waste water treatment. The resultant value was: pH value of 7.2, total carbon (TC) of 320mg/l, total organic carbon (TOC)= 311mg/l and inorganic carbon (IC) of 9mg/l.

Test on real waste water from Lyon

pH value of 7.2

TC= Total carbon= 320mg/l

TOC= total organic carbon= 311mg/l

IC = inorganic carbon= 9mg/l

Fig 4.5: Result of the analysis on real waste water

The parameter values of the synthetic waste water created for the experiments are listed in fig 4.6. The pH value was imposed at 7.2 and the acetate concentration as organic content was about 1 g/l, used as organic matter to feed the reactor of 0.7L.

Synthetic waste water experimental setup parameters

pH value: 7.2

Acetate concentration: 1 g/l

Fig 4.6: Parameters of the artificial waste water created in Lab

The process of synthetizing of the artificial solution to feed the cells and the analysis of the real urban wastewater was performed using the following equipment:

- Total Organic Carbon analyzer TOC-L *Shimadzu* for the TOC
- *Crison* GLP21 for pH

4.2.2 Single reactor

The capacitive behaviour of a WWMFC was analysed to test and improve the electrical performance of lab-scale reactors. Various experiments were performed with WWMFCs fed with urban real waste water or artificial waste water.

4.2.2.1 Synthetic waste water as fuel

In the beginning experimentations were done with a Keithley device able to impose short-circuit condition to the cell. It was used to get data of a complete discharge phase of a WWMFC fuelled with a stable *synthetic waste water* with imposed pH value of 7.2 and acetate concentration of 1 g/l.

Figure 4.7 shows a behaviour similar to that produced by a capacitor. It required a minimum of 36 hours for a complete discharge. The cell reaches a minimum value of 0.4 μA and never goes to zero. The discharge phase has a capacitive behaviour starting with a peak of 4 mA.
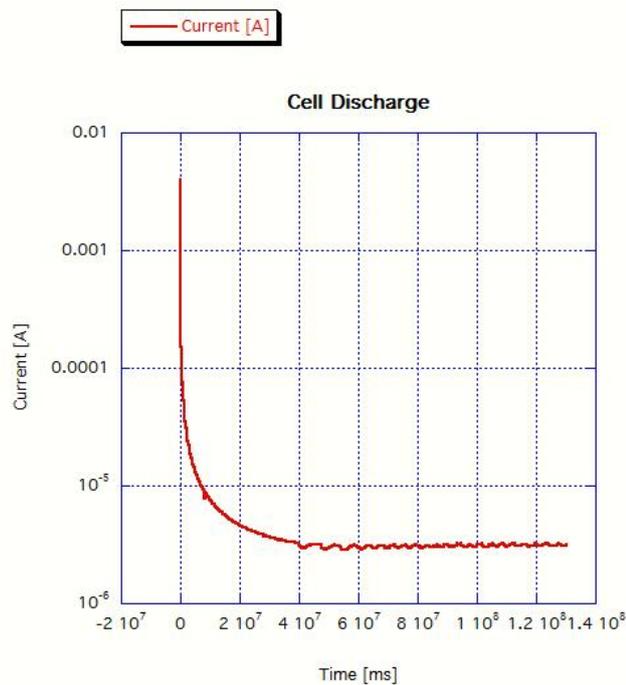
Fig. 4.7: Test of complete discharge of an operating WWMFC (36H)

Better and accurate results were obtained with the custom boards dedicated to MFC as the one designed and described in chapter 3. The reactors were fuelled

with *synthetic waste water* at stable pH value of 7.2 and acetate concentration of 1 g/l.

In fig. 4.8 and 4.9 are shown a complete discharge phase of a single cell in a time of 1 hour, imposing a zero voltage to the cell (short circuit) and the charge phase imposing open circuit. The current reached 11 μA of value as minimum after one hour of discharging (Fig 4.10).
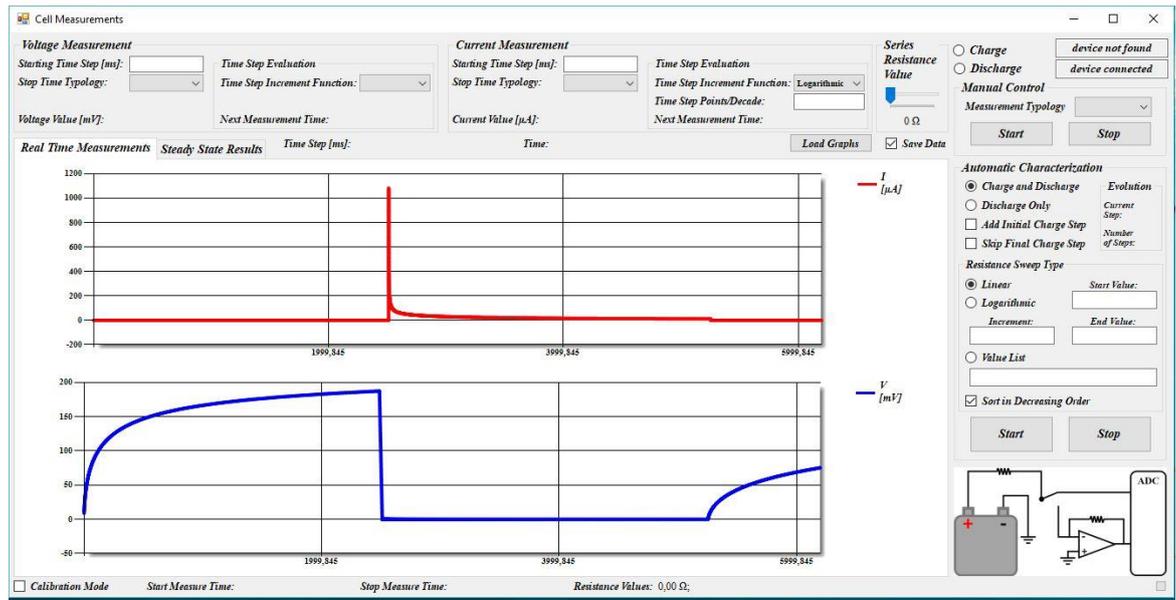
Fig 4.8: A sequence of charge and discharge phase
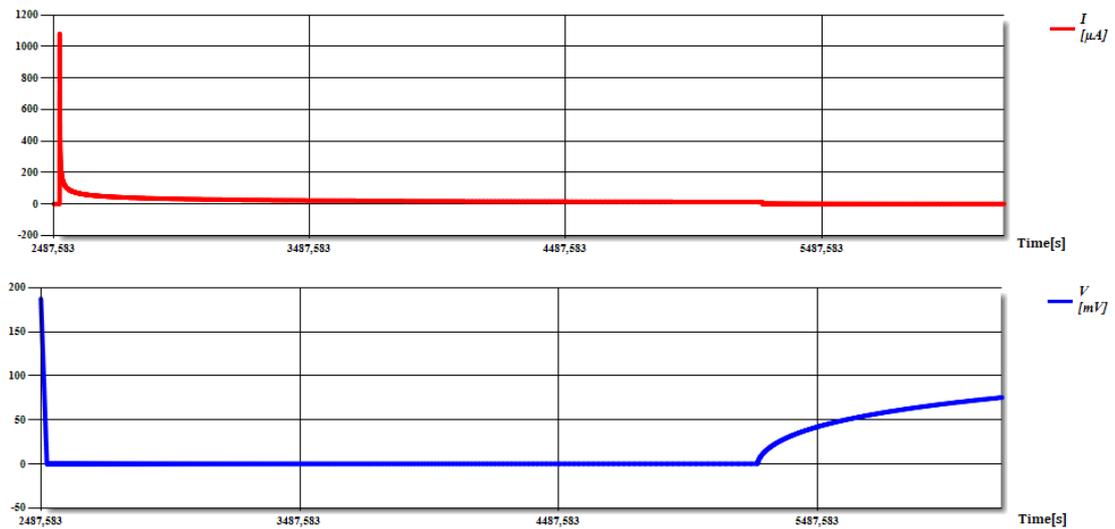
Fig 4.9: The discharge phase of a single WWMFC
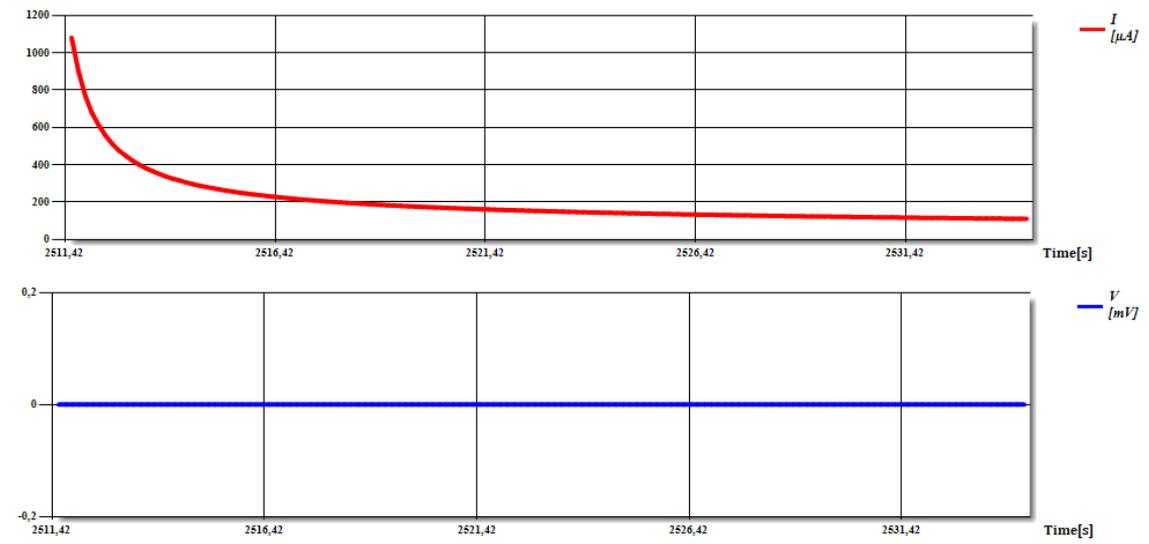
Fig 4.10: A highlight of fig. 4.9 about decay behaviour of the cell in the first 20 sec of discharge

A WSN node for monitoring can operate in sleep mode for most of the time and be activated only to transmit data. Considering that this requires a minimum transmission time, an MFC can be properly used to supply a WSN system. A low power device as a monolithic RF transceiver "Atmel ATA8510", requires less than 90 µA in sleep mode. Also, it requires as supply voltage 1.9 V, less than the 3.3 V that usually was minimum threshold needed in the last years to supply a low power device. Considering a time needed for transmission and data collection of 3s, an electrical characterization of the performance of a WWMFC was done for this time frame. The custom measuring instrument dedicated to MFC was utilized to self-collect the data. It has the feature of performing long time analysis of charge, discharge and power performance specifically for MFCs. The measurement setup for the power performance tests was done with a measurement time of 3s for each load, assuming the time value useful for WSN node operation.

After every power measurement with a certain load, the system allows the cell to reach again the open circuit voltage (OCV) before switching on the desired load value. The results of power measurement in Fig.4.11 and Fig.4.12 referred to the following load values: 110 Ω, 273 Ω, 425 Ω, 576 Ω, 730 Ω, 1 kΩ, 2 kΩ. The reactor was fed with a synthetized solution made from potable water adding a fixed concentration of 1g/l of acetate and adjusting the pH value of 7.2.

The internal resistance of the lab-scale WWMFC is around 400 Ω [29][56], in fact the maximum power point was found (MPP) at an external load value of 400 Ω. It was observed both in the case of synthetic waste water made from potable water (fig 4.11) then in the case of real waste water taken from an urban waste water center in Lyon. On the other hand, the power performance is less due to a minor concentration or shortage of various organic matters and salt in the synthetized solution, compare to a real waste-water taken from an urban treatment implant.

The level of power obtained at MPP was **27 μW** with 110 mV and 250 μA at **400 Ω**.

The maximum power point (MPP) for MFCs usually occurs at voltage levels almost equal to **50%/** 60% of the open circuit voltage. In fact, the results in Fig. 4.11 show a ratio of 55% between the 110 mV at 400 ohms and the OCV of 200mV. A proper converter should deal efficiently with the non-uniformities between MFCs and should be able to track the MPP for these different MFCs.

The capacitive behavior is described in figure 4.11 with respect to the different load values applied. Moreover, the figure shows the time required to full charge once a load has been removed. It requires a minimum of 8 minutes to fully charge after a discharge with loads applied for a measurement time of 3 second.
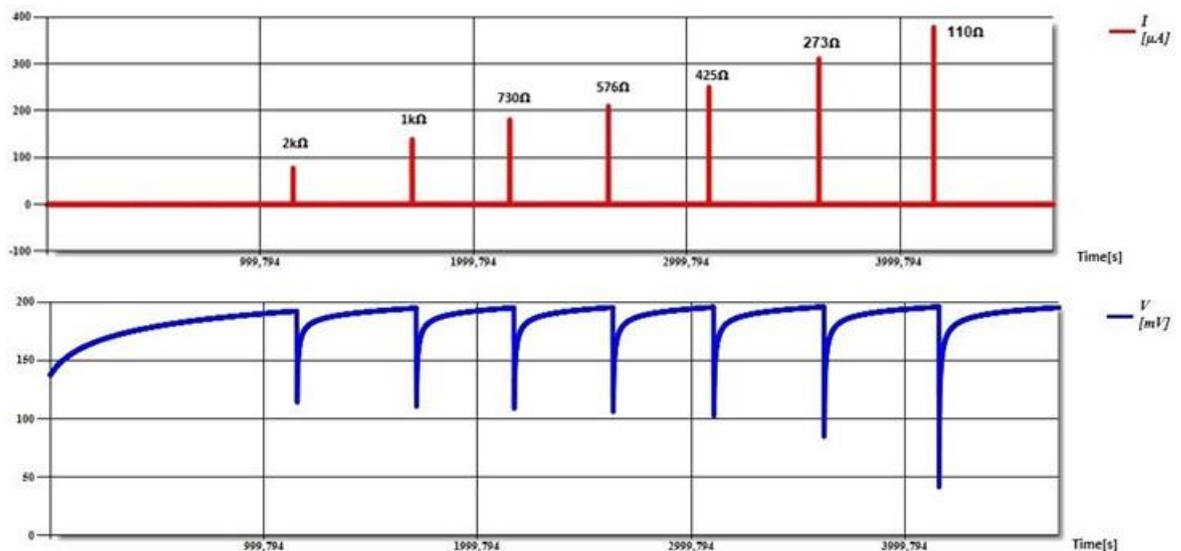
Fig 4.11: Results of I(mA) and V(mV) over time (s) of a WWMFC
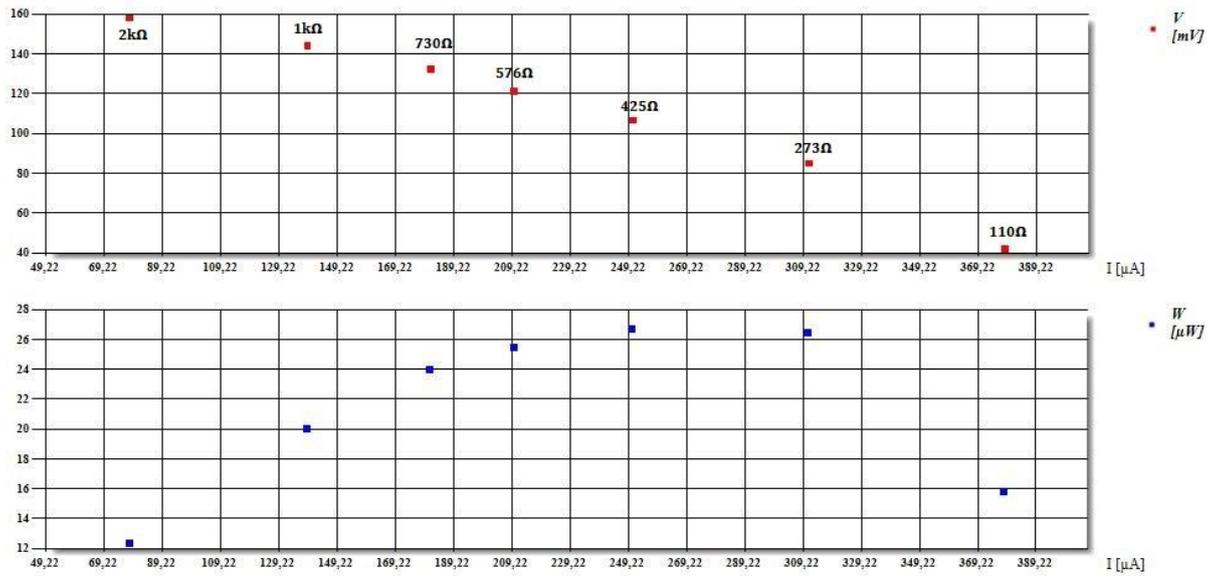
Fig 4.12: Power results for 3s measurement time with seven loads applied

A cell needs a certain time to reach again the OCV after a load is applied. This time increases when the value of the applied resistance is smaller than the previous due to a greater voltage drop. A dedicated algorithm manages this time and permits to wait until the measurement is stable. It can be set from the feature of the GUI. So, the sampling time can be set as a fixed time or can vary between measurements, in case of the automatic option chosen, to reach the stability of measure.

In Fig. 4.13 is shown the measurement system for the reactor. It is connected to a multimeter and to the custom measuring board which is connected to a computer where the graphical unit interface (GUI) dedicated to the board is running and collecting data.
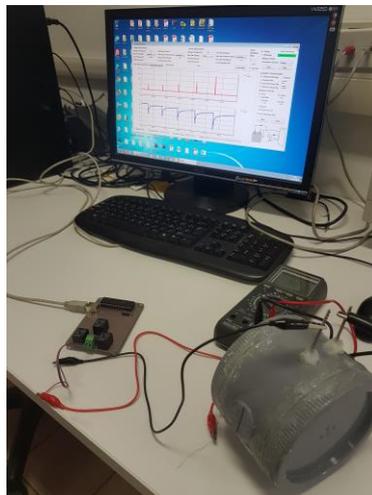
Fig. 4.13: Measurement configuration

4.2.2.2 Real urban waste water as fuel

The following figures 4.14 and 4.15 show the results with waste water collected in Lyon with another custom measuring instrument [29], for a lab scale WWWFC fuelled with 0.7l. The waste water was used after two months that it was collected from the waste water treatment in Lyon and stored in tanks in lab. An amount of 0.7g of acetate was added.

The external load covers 10 values and the measurement time for each load value was 3s. The best value of power production was found at 400 Ω and was 123 μW.
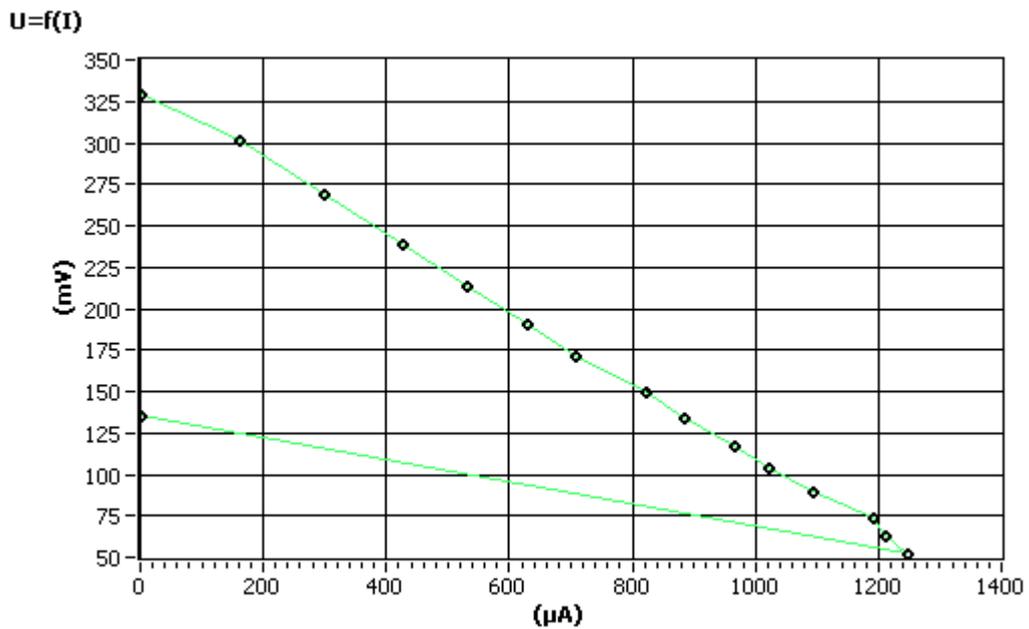
Fig 4.14 Voltage and current intensity for 10 load values
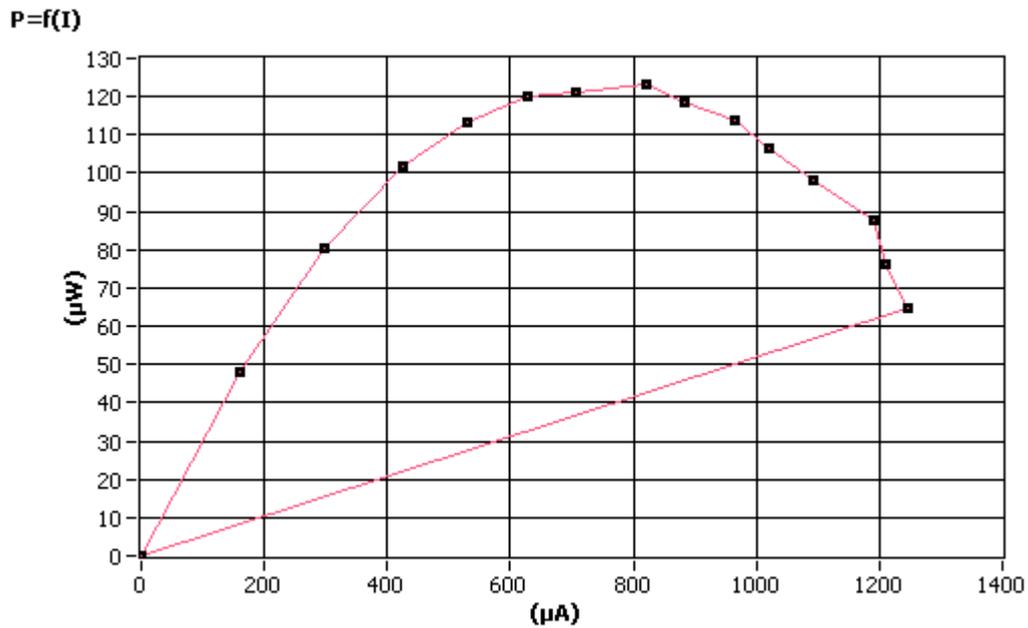
Fig 4.15 Power charts of results for 10 load values

The **temperature** is also a key factor that acts on the performance of MFCs. Temperature variation changes the conductivity of the substrate and the microorganism activity of microbial community. It was observed that there is a slight reduction in power density (9%) when the temperature was reduced from 32°C to 20°C [72]. Reference [63] recently has reported the performance of single and double chamber MFCs tested in batch mode at different operating temperatures ranging from 4°C to 35°C. The internal resistance of the MFC decreases when increasing temperature. The reason of this effect is due to the fact that ionic conductivity increases with temperature and therefore decreases the resistance [25]. Increasing temperature results in higher open circuit voltage and higher maximum power point. That can be explained by the following consideration: the higher the temperature, the higher the microbial metabolism and the higher the performance. Temperature plays a crucial factor on the biological activity and electricity production, so MFCs could be used as a temperature sensor.

A series of tests was performed in past experiments in Lyon [56] to analyze the temperature influence on the behavior of WWMFCs fed with urban waste water: the effect was studied on WWMFCs reactor by changing the operating temperature in a controlled temperature chamber ranging from 15°C to 40°C.

Experimental results are illustrated in Fig. 4.16 and show clearly that power generation by WWMFCs was significantly affected by higher temperature.
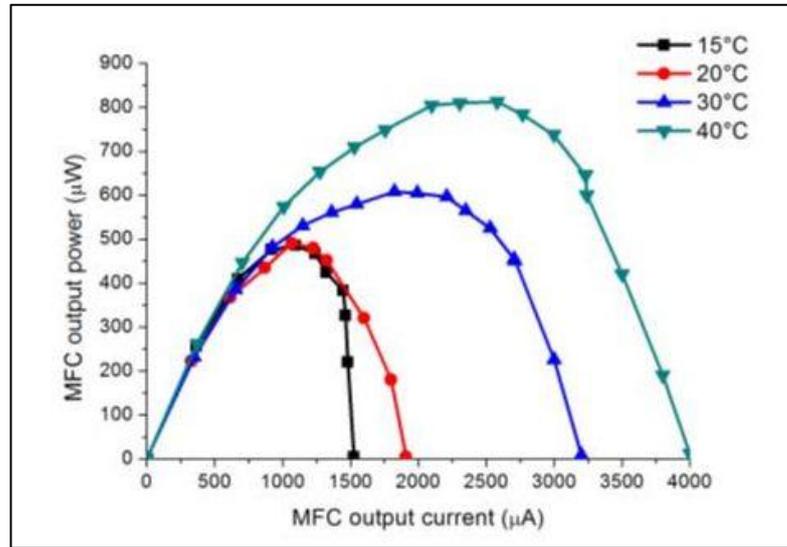
Fig 4.16: Power curves for different values of ambient temperature.

Output power curves were evaluated with maximum values of 485 μW, 490 μW, 607 μW and 812 μW for 15°C, 20°C, 30°C and 40°C respectively.

The increase in performance of WWMFCs as a function of the temperature can be explained by improving the biological activity, which will contribute to lower the internal resistance of the cells. By increasing the reaction temperature, the thermal energy available in the system is increased, which makes reactants obtaining enough energy to reach the activated state. Temperature increase is also propitious to anaerobic organisms, which then have a better environment for electricity production.

The best value of harvested power from lab scale WWMFC, fed with fresh urban waste water (taken in a waste water treatment plant in Lyon), was 812 μW at 40°C. Instead, the best result at ambient temperature of 20°C was 490 μW.

4.2.2.3 Effect of organic substrate decay

The effect of substrate acts over time because its value decreases during time. This process can be faster if the waste water is fuelling an MFC. The average open circuit voltage of a lab-scale WWMFC fuelled with urban real wastewater is 0.6 V. Usually, the value is between 0.5 V and 0.7 V in the beginning and it goes down to 0.3 V three months later due to a reduced concentration of organic substrate. As described in 4.2.1, it was observed after three months that the organic content of a real urban waste water was reduced to 0.3 g/l (311mg/l of TOC).

As described before, the best result at ambient temperature of 20°C was 490 μW for a reactor fueled with fresh urban real waste water.

Instead using the same waste water but after two months, the value of power at MPP achieved during tests of 3s of measurement time was 123 μW.

Also, for a synthetic waste water created in lab the effect was monitored during time. The value of acetate as organic substrate was 1g/l for the artificial water. The average of OCV value was monitored around 300 mV with an output power of 36 μW and reduced down after one/two months at 200 mV and a power of 27 μW at MPP (measured during 3s on a 400 Ω load).

4.2.2.4 Effect of pH

An experimental campaign was done on WWMFC reactors to study the effect of **pH** on energy conversion performance. The results (Fig. 4.17) show a slight effect of the pH value on WWMFC, when compared to TMFC. The pH value of the soil has a critical influence on TMFC, instead in a WWMFC with a solution of pH value between of 6.5 and 7.5 the effect on energy production seems not to be great. The WWMFC used in the experiments was fuelled with the synthetic waste water made with the technique described before: four lab-scale reactors were tested with different imposed pH values: 6.5, 7, 7.2, 7.5.
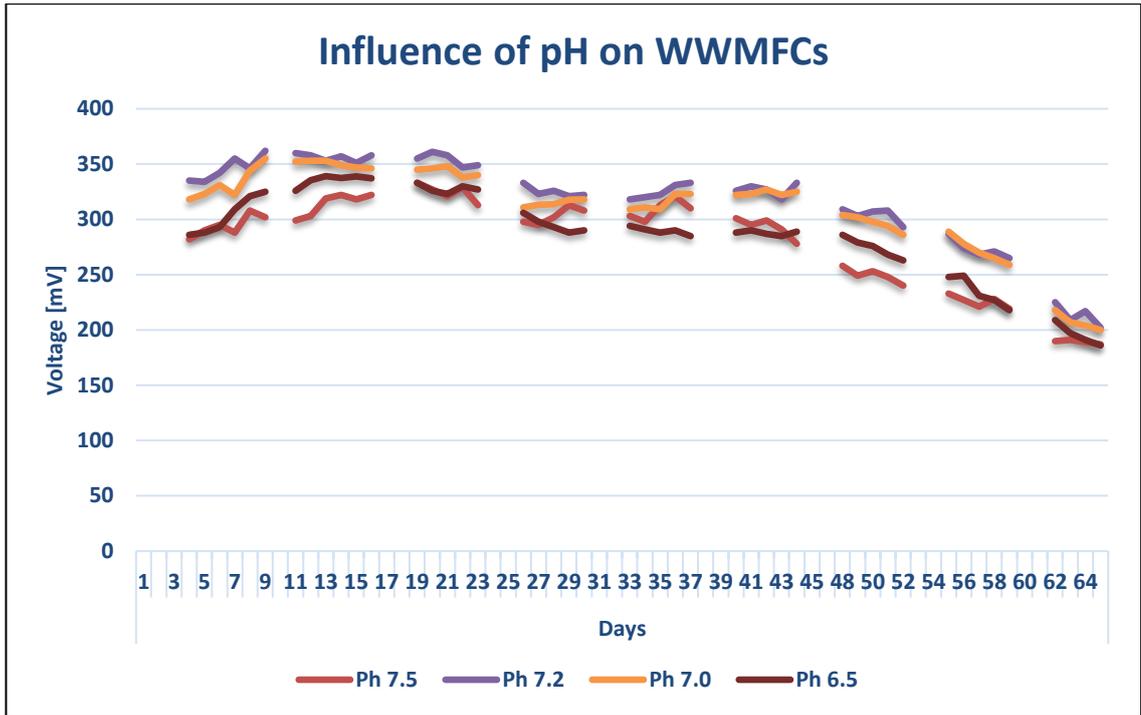
Fig 4.17 pH influence on OCV of WWMFC

4.2.3 MFCs arranged in form of a pack

Concerning WWMFC applications, it was arranged WWMFCs in the form of pack devices in order to use them as a small power generator. Pointing to a massive utilization of bioreactors as energy source like a small power generator, it was performed a series of tests to study the best configurations for multiple connections of WWMFCs.

Multiple connections of bioreactor can lead to a greater energy production with respect to a big size single reactor. The increase of reactor's size does not lead to an improvement in performance because of the distance between electrodes. Therefore, it was performed a series of tests to analyze the performance of WWMFCs in multiple connections with different configurations as series and parallel for two or more cells.

4.2.4   Parallel configuration

A decrease in internal resistance was observed that occurs when two reactors are put in parallel configuration: MPP was found at an external load of **200 Ω**. The reduced value of internal impedance can bring better performances in term of power and current delivered due to the reduced ohmic drop. The ohmic losses is the linear resistance to the flow of electrons through the material of the electrodes and the various interconnections, as well as the resistance to the flow of ions through the electrolyte

The maximum power of 112 µW at MPP was found at 200 Ω, as represented in Fig. 4.18. The figure shows the value of power for 8 different external load values applied from 100 Ω to 800 Ω. It delivered 148 mV and 600 µA at MPP in parallel configuration. The value of power from two WMMFCs in parallel configuration was increased with respect to the value of a single reactor. In fact, the internal resistance was decreased to half the value of a single WWMFC, from 400 Ω to 200 Ω. Also, the current intensity had the same improvement.

The parallel configuration can be considered as an interesting way to use MFCs arranged in a form of cluster to increase the value of current and power.
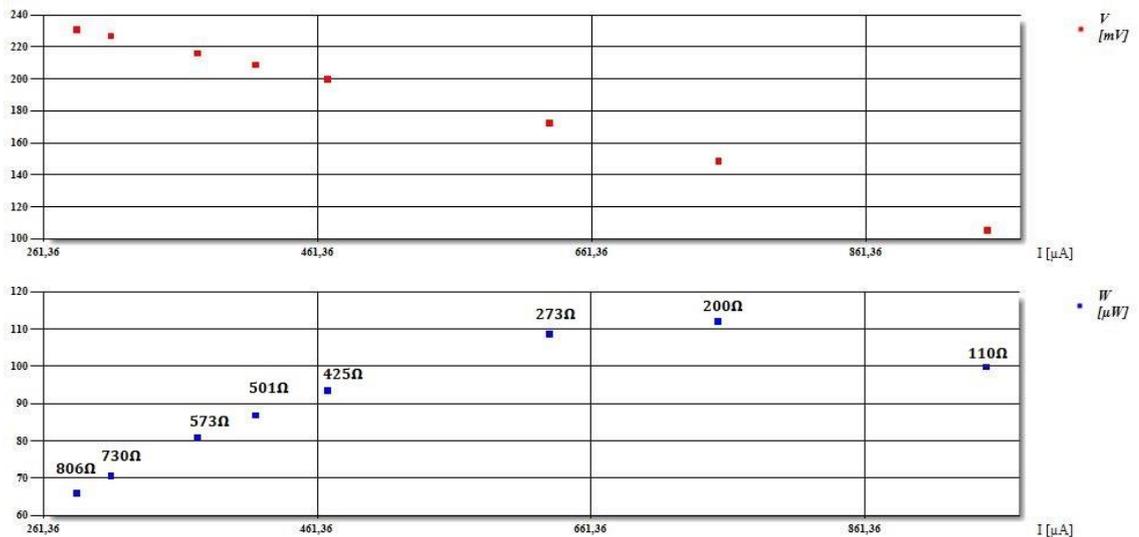
Fig 4.18: WWMFCs in parallel configuration power chart

4.2.5 Series configuration

Series connection of two WWMFCs was experimented using the custom instrument board in Rome described in chapter 3. The results show the electrical behaviour of a stack of two cells in series connection.

In Fig 4.19 is represented the electrical charge after the moment when the two cells are connected in series: it shows the capacitive charge between 275 mV to 510 mV during 1300s. The WWMFCs used were fed with synthetized waste water and the voltage of each reactor was different. One MFC_1 has an OCV value of 330mV and the other one MFC_2 a reduced value of 190mV, due to a solution used from two months with decreased substrate.

Anyway, the connection brings the final OCV to a value of 510mV as shown in Fig. 4.19, similar to the sum of the value of the MFC_1+MFC_2 as expected.
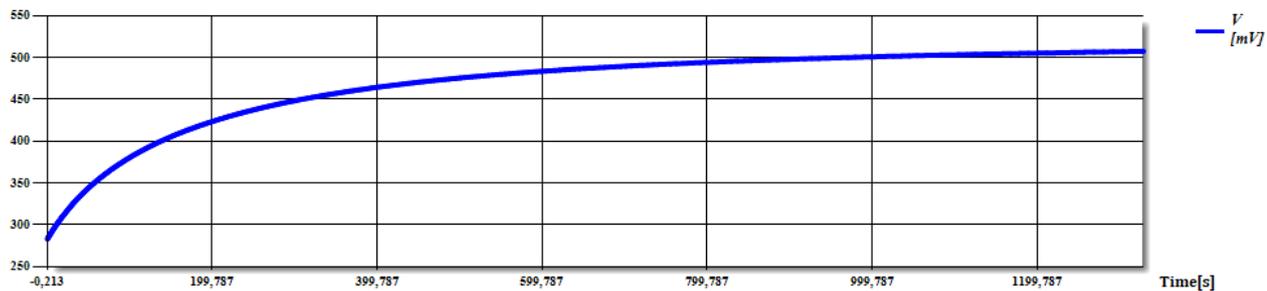
Fig 4.19: OCV during time until stabilization

4.2.5.1 Connection of multiple MFCs

Experiments with a large number of MFCs was done with WWMFCs arranged in series configuration, fed with *urban real wastewater* after 3 months it was taken, so with decreased organic content, but with the addiction of 0.7g of acetate directly in the reactor.

Fig 4.20 shows the results for serial connection of 6, 10, 16, 20 and 25 reactors. The results in the figure are an average from experiments done with WWMFCs reactors fed by real urban waste water.

The experimental setup was done with the measuring board in Lyon. The 25 cells have average OCV value of 250 mV in single configuration.

The OCV value of six reactors in series connection has reached a value of 1.46 V, instead for ten cells arrives up to 2.55 V. The value of the open circuit voltage for sixteen cells in series connection was 3.64 V and for twenty reactors 4.68 V. In the case of 25 cells in series connection, the value of OCV raise up to 5.72 V.
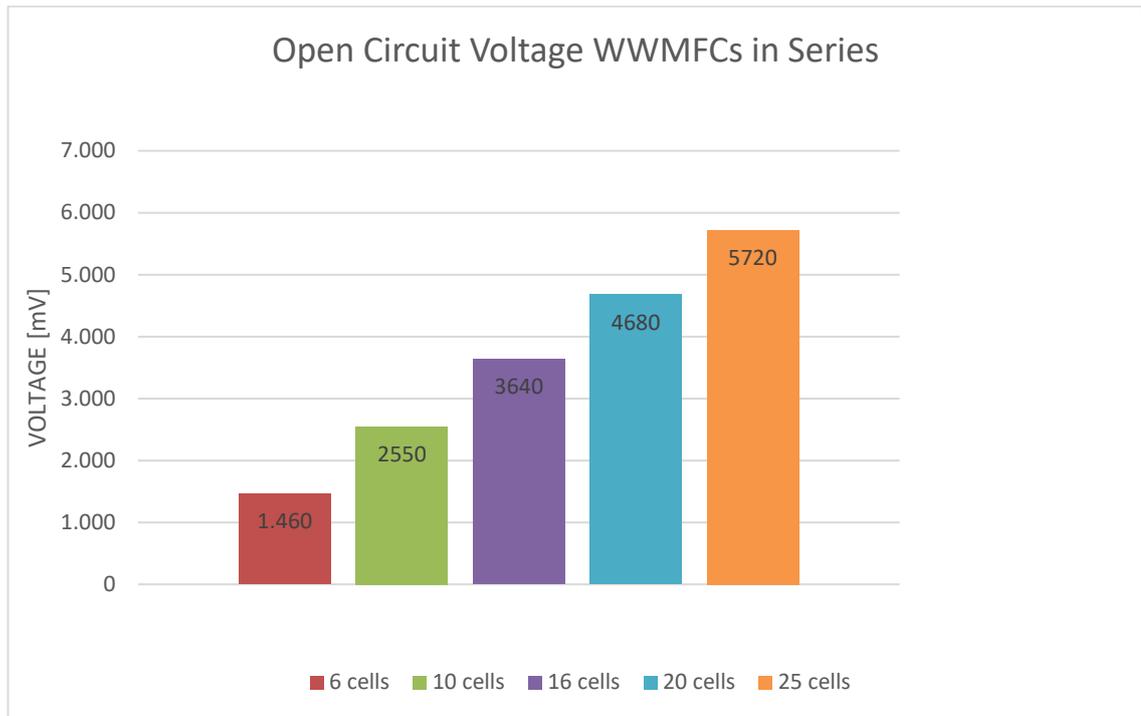
Fig 4.20: Chart of series connection of WWMFCs up to 25 reactors

When MFCs are in a stack in large number, for current intensity analysis some issues can arise as problems of short-circuit, bad connections, long cable resistance. Also, it is mandatory to use of a proper system able to monitor high voltage reactors in connection as 10V/30V, bigger than the measuring instruments present in Rome and Lyon (1.2V/2V max).

An efficient system for a large stack of MFCs should minimize the cell geometry and the stack geometry. The space occupied by cells should be minimized as the length of wires, to avoid drops and short-circuits.

4.2.6 Reversal voltage: polarization of MFC

During experiments, it was discovered a way to improve electrical performance boosting the power delivered by MFC. Applying a voltage as 2V to the cathode forces a flow of electrons into the electrode: this leads to an improvement in the growth of bacterial population. The *Shewanella bacterial strain* shows a more developed population in place of *Pseudomonas bacterial strain* as confirmed from the studies done by the microbiology research group of Surrey University (as Avignon-Rossa and Nastro).

An MFC has a *capacitive behaviour*, its cathode electrode is able to accumulate charge and discharge as a classical capacitor. The characteristic of this capacitive behaviour depends on many factors as structural, environmental and on the fuel.

During experiments another phenomenon was observed: in the moment that two WWMFCs are disconnected from a parallel stable configuration: both of reactors have been found at the same open circuit voltage (OCV) level. Reactors can clearly influence each other and is evidently how they can withdraw or release charge as a capacitor.

Starting from that and considering these phenomena, a new experiment was set up. One reactor was connected to the cathode with a digital supply device as external voltage source set at **2 V**.

At the moment of the connection, a current of 0.4 A instantly flows in the reactor from the digital source and immediately the open circuit voltage reached the voltage value of 2 V imposed. It was monitored on-line with a digital multimeter.

In terms of time, the charge phase of the reactor was **immediate**; after that the WWMFC doesn't continue to draw any current and the digital supply shows a current level of 0 A. At this point the voltage is still at 2V until the digital supply is disconnected.

When the disconnection between the external voltage source and the cell was carried out, immediately the cell voltage starts to decrease, so the open circuit voltage of the reactor beginning to discharge with a capacitive behaviour.

The discharge phase was monitored with the custom measurement instrument as in Fig. 4.21.
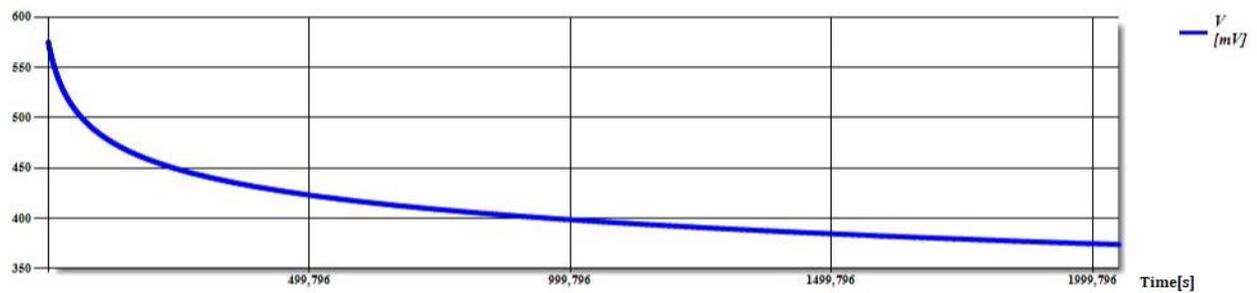
Fig 4.21: Discharge phase of the cell after polarization method was applied

The discharge phase was monitored in fig 4.22 for 30 minutes. The value of open circuit voltage was 451mV and reaches the value of 324 mV in 1800 s. The voltage decreases as a capacitive behaviour of 126.8 V in a time of 30 minutes.
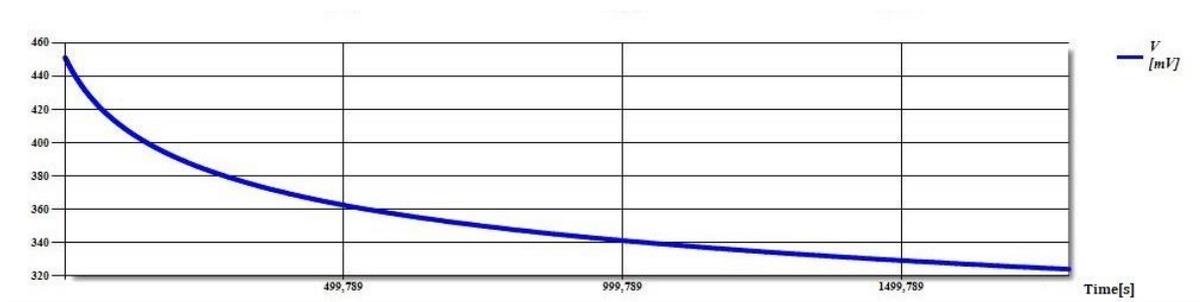
Fig 4.22: Discharge phase of the cell tested during time for 1800s

At the end of the discharge phase the voltage usually reaches an average level of 330mV better than the previous one before applying the voltage polarization method.

It was observed that, the voltage returned to a greater level than at beginning and the current generation was improved. It led to a better performance in terms of power delivered by the WWMFC. Considering that the theoretical maximum voltage which an MFC can usually produce is equal to 1.2V, other experiments were performed with 5V or 1.5V imposed showing the same behaviour, with this values is sure to bring the cell at is maximum value of possible voltage production.

An experimental campaign was done on WWMFCs in single (fig. 4.23) or parallel configurations fuelled by stabilized synthetic wastewater made from laboratory of chemical engineering.

The single reactor reaches a power value of 58 µW at 125 mV and 500 µA. The results are higher than the power value of 27 µW reached with a single reactor in the same experimental condition and measurement set up shown in fig 4.12

With respect to experiments done with same reactor model, environment condition and fuel, the results show an improvement of the generated power. The WWMFCs show an increased performance in terms of energy conversion from chemical to electrical due to an excited state of bacteria after the process. This should lead to a growth of the bacteria proliferation on the electrode.
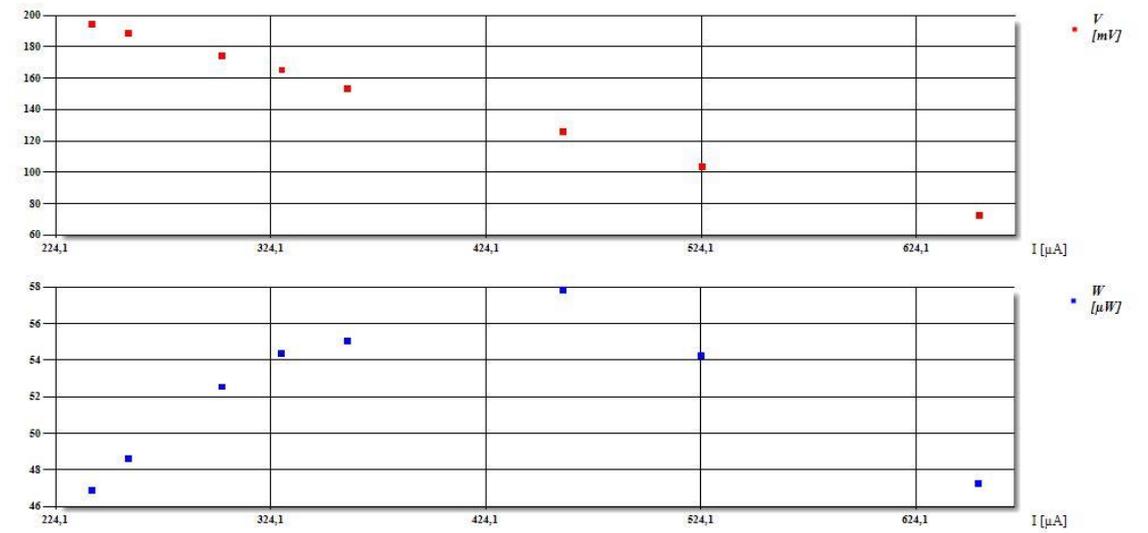
Fig. 4.23: Results of power analysis (3s) of a single reactor after polarization applied

Other experiments were done with a **3 minutes** of measurement time as described in figures 4.24 and 4.26. The power delivered at 400 Ω (MPP) was almost 10 µW after 3 minutes, a high value for a reactor filled with synthetic waste water. The difference can be evaluated from the figures 4.25 and 4.27 that represent the values of voltage current and power delivered by the same WWMFC before the experiment with external voltage of 2V was applied.
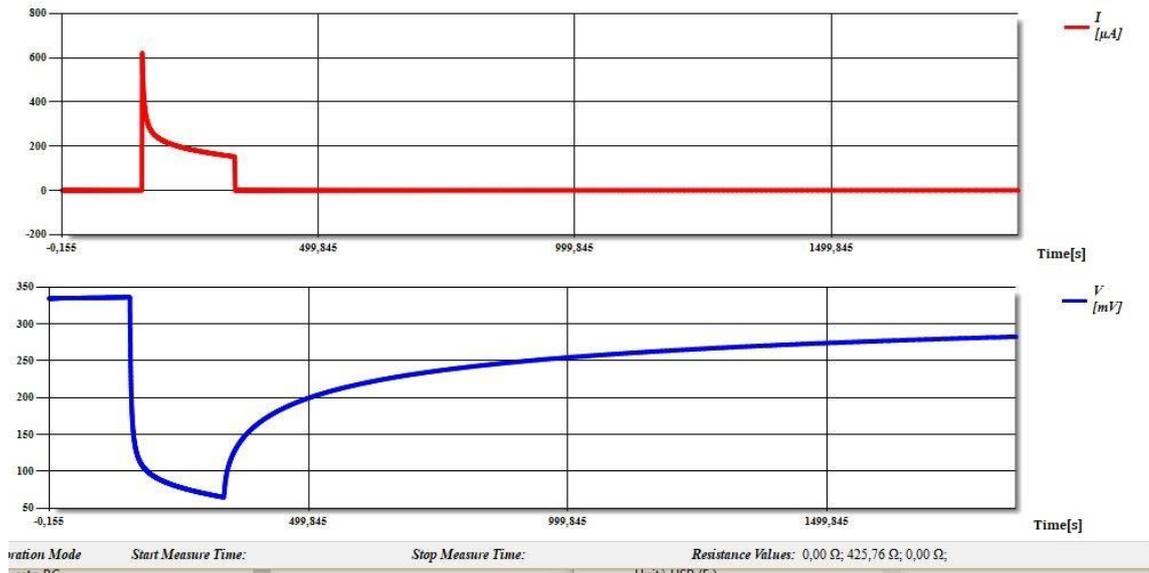
Fig 4.24: Results in term of voltage and current delivered during time (3 minutes measurement time) for a WWMFC after polarization method applied
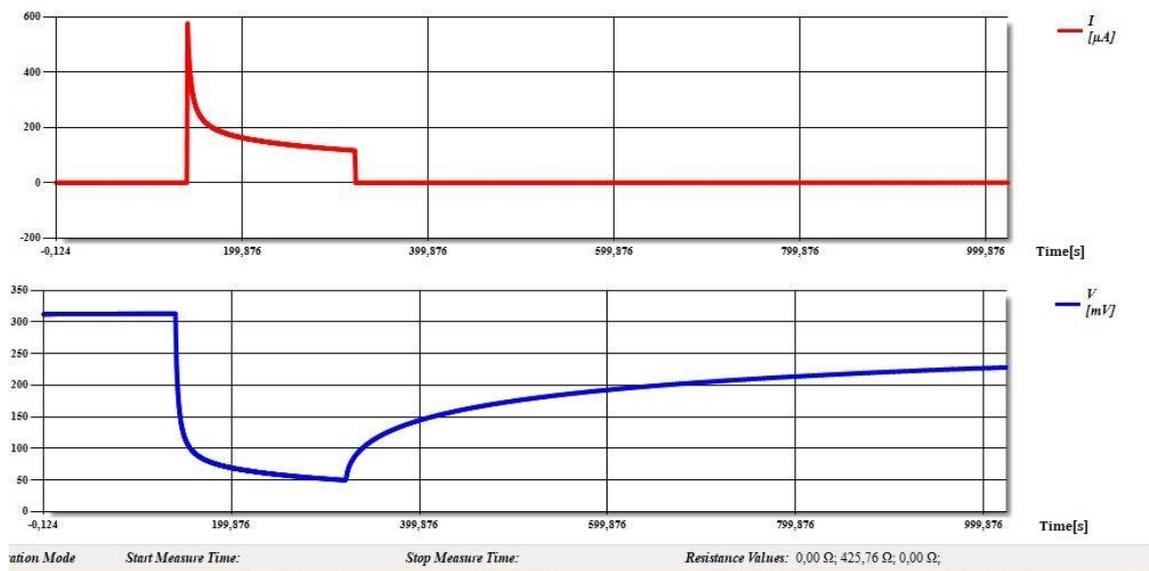
Fig 4.25 Results in term of voltage and current delivered during time (3 minutes measurement time) for a WWMFC before polarization method applied

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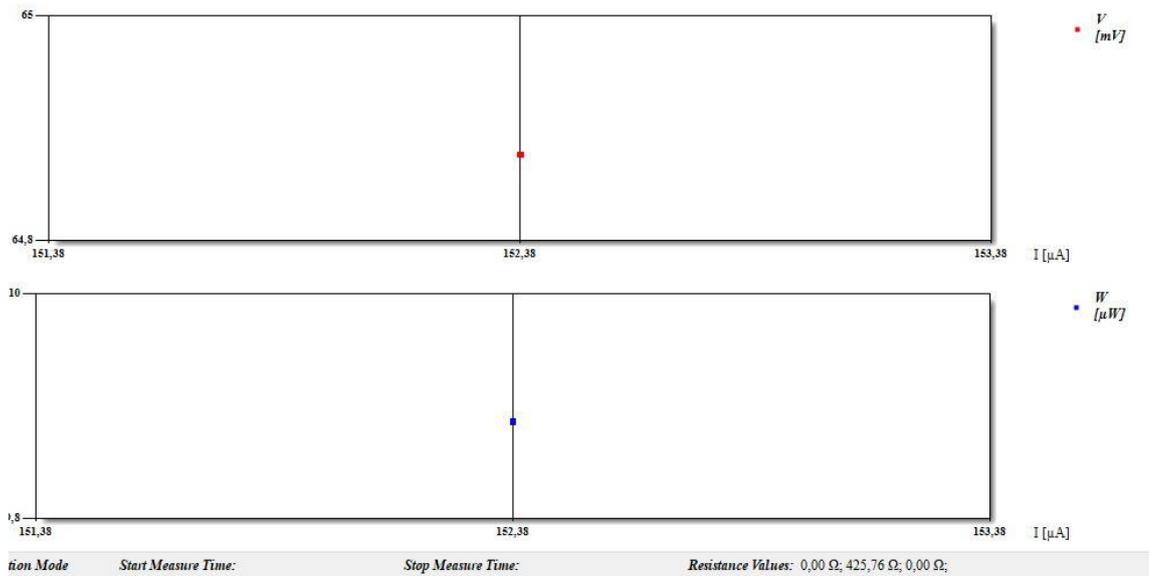
Fig 4.26 Power chart result for 3 minutes as measurement time for a WWMFC after polarization method applied
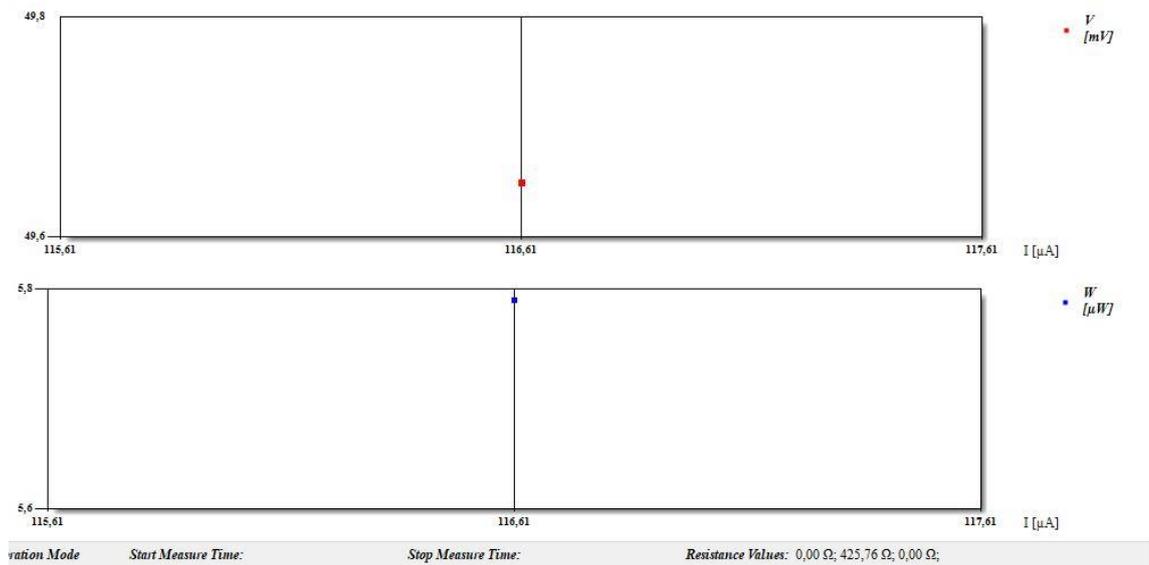
Fig 4.27 Power chart result for 3 minutes as measurement time for a WWMFC before polarization method applied

In Fig. 4.28 a parallel **connection** of WWMFC was experimented in the same way, applying an external voltage source of 2V on the reactors. The measurement was performed with **3 s** of maintaining time. It has been done only waiting after the time needed for cells to discharge, considering of the high voltage value reached.

The results show an advancement with respect to similar experiments done without the external source applied: the power produced goes up to 140 µW better

than the 112 µW shown in figure 4.18. for the same measurement time of 3s, as a WSN active node could need.

The **decrease in internal resistance** will occur in parallel configuration also after imposing a voltage on cathode: MPPT was found at **200 Ω** as *internal resistance* with 140 µW of power.

In this way, two WWMFCs in parallel configuration, though with a stabilized synthetic waste water made from potable water with reduced performance, in place of a real urban waste water, can deliver a considerable amount of power able to easily empower an ultra-low power sensor or a node of a WSN with the proper energy management system.
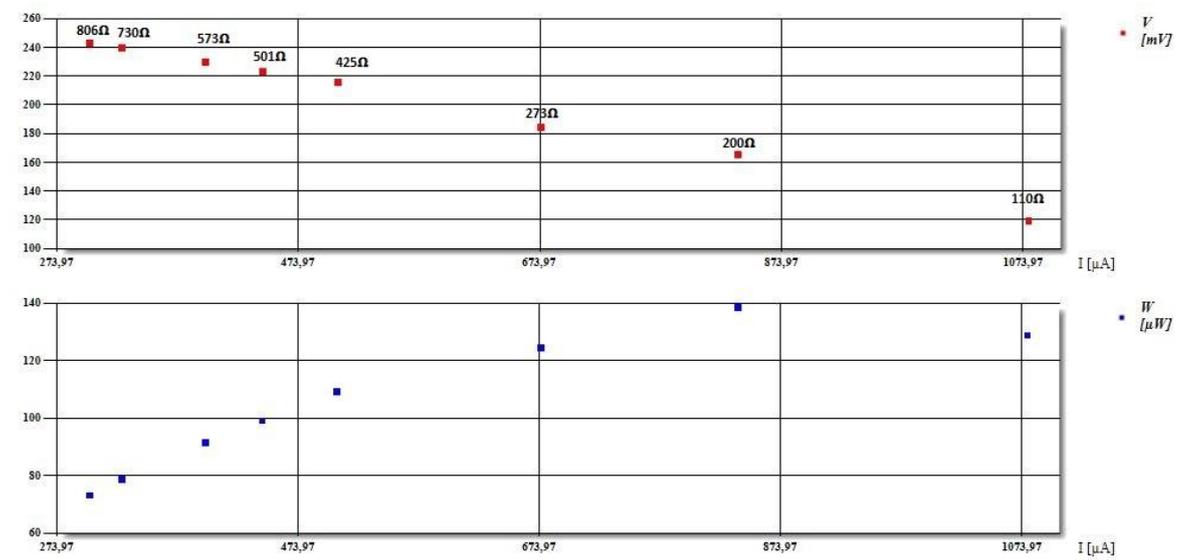
Fig. 4.28 Results of power production with 8 values of load applied: results of I(mA) and V(mV) over time (s) of a WWMFC

5. MFC APPLICATION

Harvesting energy from available sources is an effective solution for powering ultra-low power devices. Due to its properties, MFC could be useful to many different applications. As a matter of fact, the energy converted by MFC can be utilized in a wide range of domains. One can consider powering a node of a WSN, allowing the realization of applications such as continuous monitoring like in precision farming without environmental impact. Every network node includes a transceiver for communication and generally a microcontroller for local operation and signal processing [1].

5.1 Field of application

Usually, these devices require a minimum voltage of 3 V or less for proper operation. Considering low levels of voltage and current delivered by MFC, an interface circuit is needed to increase the voltage level and to accumulate the amount of electrical charge required for system operation. In this case system operation is not continuous but many applications support this operating mode. As an example, a WSN could only work in the short time required for collecting, transferring and storing environment information. Thus, a power management system includes a step-up DC/DC converter to boost voltage and to support the proper operation of WSN node [1][99].

In wastewater treatment plant (WWTP), a high efficiency can be obtained as wastewater is rich in organic matter such as sanitary waste, food processing wastewater, swine and corn stove wastewaters [124]. Furthermore, it is possible to use MFC as a biosensor [33], for example to measure the biological oxygen demand [79] or water quality monitoring [22, 32]. Generally, each network node of a wireless sensor network includes a sensor device to collect information from the environment and transmits data to the central node. Therefore, the use of MFC as a biosensor device and not only as a power supply allows minimizing the environmental impact of a network node.

5.2 Energy management system to supply WSN

Each node of a wireless network includes a transceiver for communication and a microcontroller for local management of the information. An MFC delivers current and voltage values that are lower than those needed for the operation of these devices. In order to reach adequate levels of current and voltage, an energy management system is required.

Since MFCs produce a level of voltage not enough to support what a WSN node requires, it is needed to store the energy during the standby/idle time of the system. The operation mode of "energy storage" is needed until the stored energy reaches the amount required to support the proper operation of WSN node, does it mean the data elaboration and transmission. For these reasons, the design of power management system includes a step-up DC/DC converter to boost voltage.

The energy produced by TMFC can be used to power a node of a WSN, allowing the realization of applications such as ambient monitoring and precision farming without environmental impact. Every network node includes a transceiver for communication, and generally a microcontroller for local operation and signal processing.

The electric current required by these type of devices changes depending on the specific operating while the voltage level necessary for the operation is equal to 3.3V, but this level is ever reducing. The transmission devices included in a network node powered by MFCs, and chosen according to the communication protocols used, must necessarily be ultra-low consumption. Possible solutions are the IEEE 802.15.4 standard communication protocol, as ZigBee protocol, and the IEEE 802.11 standard protocol, e.g., Wi-Fi. Also, wireless personal area network (PAN) technology as Bluetooth Low Energy (BLE) 2.4GHZ can be also a suitable solution. Another wireless data communication technology useful is **LoRa** (**Lo**ng **Ra**nge) which uses license-free sub-gigahertz radio frequency bands like 169 MHz, 433 MHz, 868 MHz (Europe). LoRa is a modulation technique developed by Cycleo in Grenoble and enables very-long-range transmissions (more than 10 km in rural areas) with low power consumption [80].

5.2.1 Comparison of DC/DC converters and transceivers for WSN

In the following table 5.1 is a comparison of principal properties and voltage requirement for some low power converter. The converters LTC 3108 and LTC 3105 by Linear Technologies are presented with the Enocean ECT 310 DC/DC converter. Moreover, the S-882Z, which has a start-up input voltage of 300mV is produced by Seiko.

Instead, the BQ25504 by Texas instruments is a boost converter which can be started with V_{IN} as low as 330 mV but once started, can continue to harvest energy down to V_{IN} = 80 mV. Also, it has an integrated programmable dynamic maximum power point tracking (MPPT). The TSP61221 by Texas instruments has an efficiency of 0.9 and an input voltage of 700mV.

Energy harvesting DC/DC converter comparison				
Converter	**Start-up V_{IN}**	**V_{OUT}**	**MPPT**	**Efficiency**
LTC 3108	20mV	2.35/3.3/4.1/5V	No	0.6
LTC 3105	250mV	1.6V to 5.25V	Yes	0.6
ECT 310	20mV	3V to 5V	No	0.3
S-882Z	300mV	1.4V to 2.4V	No	0.2
Pollak [99]	70mV	2.5V to 5V	No	0.7
TSP61221	700mV	1.8V to 6V	No	0.9
BQ25504	330mV	1.8V to 5V	Yes	0.8

Table 5.1: Energy Harvesting low power DC/DC converter comparison

In the following table 5.2 is shown a comparison of commercial transceiver devices necessary for a node of a WSN. It shows the main characteristics of the transceivers as the active Tx current required in transmission and sleep mode current consumption, supply range and frequency used. Also, it is indicated if a microcontroller is integrated in the low power RF system.

Device [Protocol]	ActiveTx (I)	Supply Range	Frequency	Sleep Mode (I)
Nordic nrF24LE1 [802.11]	11.1 mA	1.9 V to 3.6 V	2.4 GHz	550 nA
CC2533 [802.15.4]	28.5 mA	2 V to 3.6 V	2.4 GHz	1 μA
CC1310 [802.15.4g]	13.7 mA	1.8 V to 3.8 V	686 MHz	7 μA
RN313C [802.11/Wi-Fi]	210 mA	2 V to 3.3 V	2.4 GHz	4 μA
Enocean STM312 [802.15.4]	100 mA	2.1 V to 5 V	868 MHz	4 μA
XbeePRO S2B [802.15.4 ZigBee]	233 mA	3.1 to 3.46 V	2.4 GHz	4 μA
MRF24J40MA [802.15.4]	23 mA	2.4 to 3.6 V	2.4 GHz	2 μA
ATMEL ATA8510 [802.3]	9.4 mA	1.9 V to 3.6 V	868 MHz	600 nA

Table 5.2: Comparison of low power transceivers for WSN nodes empowered by MFCs

The transceiver systems by Texas Instruments are the CC1310 Wireless MCU containing an ARM Cortex-M3 (CM3) 32-bit CPU and the CC2533 combines the performance of RF transceiver with a single-cycle 8051 compliant CPU.

The CC2533 is an optimized system-on-chip (SoC) solution for IEEE 802.15.4 based remote-control systems as ZigBee. The RN131C, the ATMEL ATA8510 and the MRF24J40MA are produced by Microchip.

5.2.2 WSN powered by TMFC

As mentioned above, the interface circuit must generate sufficient power for supplying a WSN node during the operating phases characterized by higher consumption, such as the transmitting phase. Therefore, normally the circuit includes a boost converter for power management.

In literature, there are two main ways to address the problem: a first method, which uses a configuration that provides for the presence of a transformer in the step-up converter, and a second method which instead using a transformer-less configuration. In the one with transformer [1], the start-up circuit uses JFET rather than a MOSFET, because JFET's gate cut-off voltage is very low compared to the MOSFET's one (Fig. 5.1).
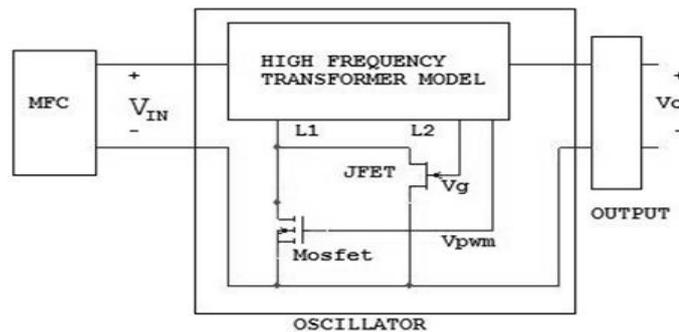
Fig. 5.1: Converter scheme: configuration with a transformer.

Moreover, JFET's gate capacitor is so small as to reduce the switching losses. However, DC/DC converter with a transformer does not use JFET as principal power switch, because a high value of its drain-source on-resistance (R_{ds}) increases converter losses. As a matter of fact, most converter losses are due to the JFET, unlike those of the transformer that are negligible. In this configuration, the conversion efficiency is expected to be about 65% in the case of an input power of

310 μW supplied from lab scale-TMFC. In the other configuration without a transformer [94] [95], for implementing the DC/DC converter, the energy harvesting electrical scheme uses essentially a two-stage circuit (Fig. 5.2). They are two feedback converters, the first one dedicated to energy harvesting conversion, the second one to output voltage boost transformation.

The latter configuration is without a transformer, but in order to properly operate the comparator, included into the controller section of harvesting and boost, it must be provided the use of reference voltages and power values that could be greater than those produced by the MFC. It is the preferred solution when input voltage is higher than about 250 mV.
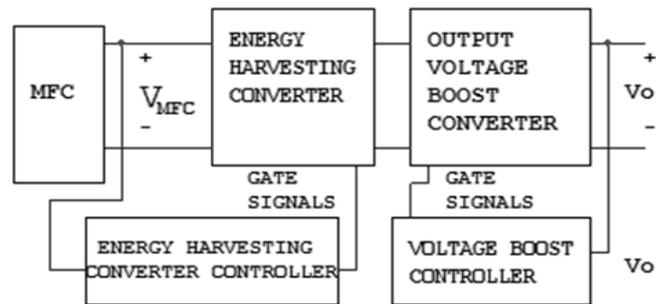
Fig. 5.2: Two-stage transformer-less converter.

Adopting the step-up DC/DC converter circuit implemented in [31], based on a model with transformer, the circuit was optimized in order to make it suitable to TMFC (Fig 5.4). The converter is optimized for an input voltage from 0.6 V. (Fig. 5.3), corresponding to the supply voltage of a lab-scale TMFC. In this configuration the converter however requires an excessive amount of current.
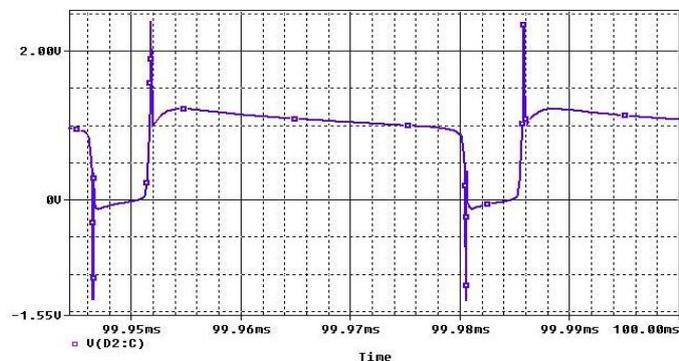
Fig 5.3: Step-up DC/DC converter optimal duty cycle experimental system (simulation).
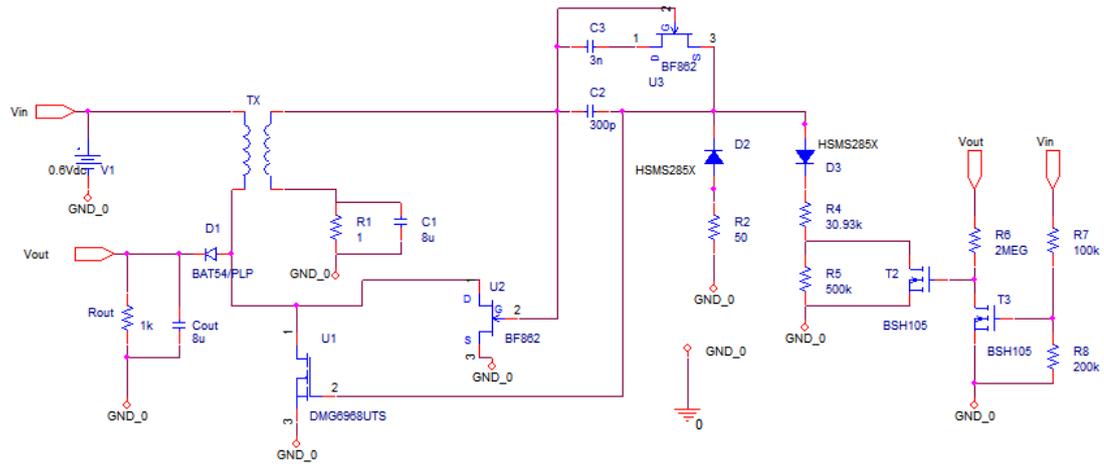
Fig 5.4: OrCAD schematic of the adapted circuit for TMFC

A series of transformer-less converter configurations using commercial converters, like LTC3105 by Linear Technology Company or TPS61221 by Texas Instruments was observed. The **TPS61221** need **0.7 V** as input voltage for a proper operation.

In order to limit the inrush current to the one generated by TMFC, whose maximum value is 0.5 mA, it is required to design a circuit with a capacitor for storing the energy before the converter block, which includes the commercial DC/DC.

A simplified block diagram is shown in Fig. 5.6. It includes a first stage to store the energy charge, a second stage with a step-up converter and a final output stage with load connection.

In the first stage, during an established time, a source with limited value of supply current (0.5 mA) charges a capacitor with value of 6.8 mF. The duration of charge interval is a function of the WSN operating characteristics.

At the end of this time the capacitor will have accumulated an amount of charge such that the voltage across its terminals is equal to about 700mV. An integrated TPS61221 was used as a converter inside the second stage and an output capacitor with a value of 10 μF.
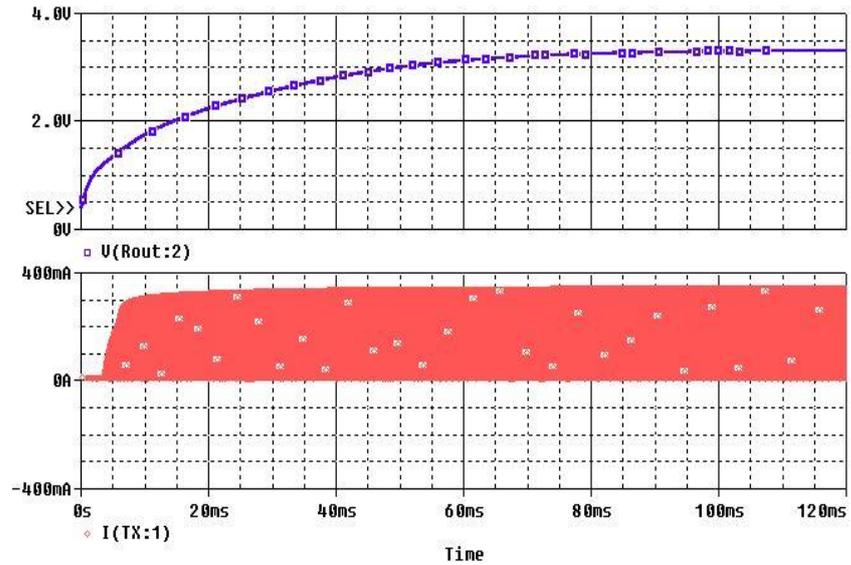
Fig 5.5: The output voltage of stage two reaches 3.3 V.
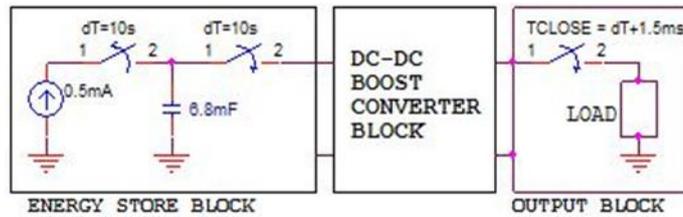
Fig 5.6: Block diagram of the proposed system with TPS61221 inside converter block

After the charge time, the capacitor like a backup battery of about 700 mV, supplies the converter block, whose output voltage reaches 3.3 V after a time of 1.5 ms.
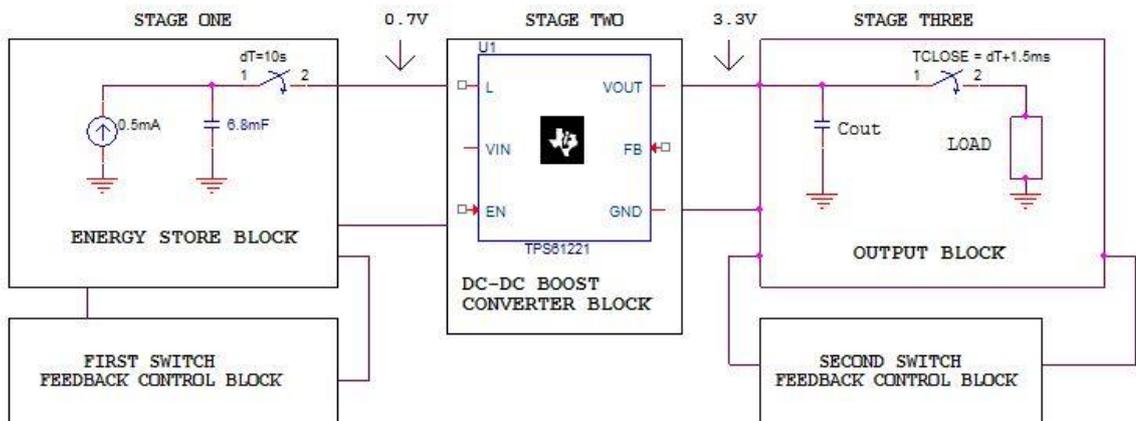
Fig. 5.7: Three-stage block diagram, the second switch in the output block close the circuit after a time of ΔT+1.5ms to connect and supply the load

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The first block needs an output switch that connects the first stage to the second one at the end of capacitor charge interval, when the amount of charge is adequate for proper operation of a commercial converter. In this way at the end of the charge-time, the capacitor acts like a backup battery of about 700 mV that supplies the converter block. Normally it can use a p-channel MOSFET as output switch, but it needs a control on gate terminal.

For this reason, a feedback control block is added in Fig 5.7, which activates the transistor, i.e. it closes the circuit, by acting on the gate voltage. When the output switch of first stage closes the circuit, the TPS61221 starts to boost the voltage from 0.7 V to 3.3 V in a time estimated equal to 1.5 ms (Fig 5.5).

After this period, a second switch, present in the last output stage, has instead the task of closing the circuit to connect the load, when capacitor functioning like backup battery is capable to supply the energy to the same load during the operating time. The second switch also requires a control loop in order to modify the voltage of the gate terminal and to close the circuit at the appropriate time. The output load emulates an interface circuit with transceiver of a WSN node.

It is possible to see in Fig. 5.8 from top to bottom, the results of the simulated current and voltages. In particular, the current drawn by input capacitor; the decrease in voltage on the same capacitor and the increase in output voltage up to 3.3 V.
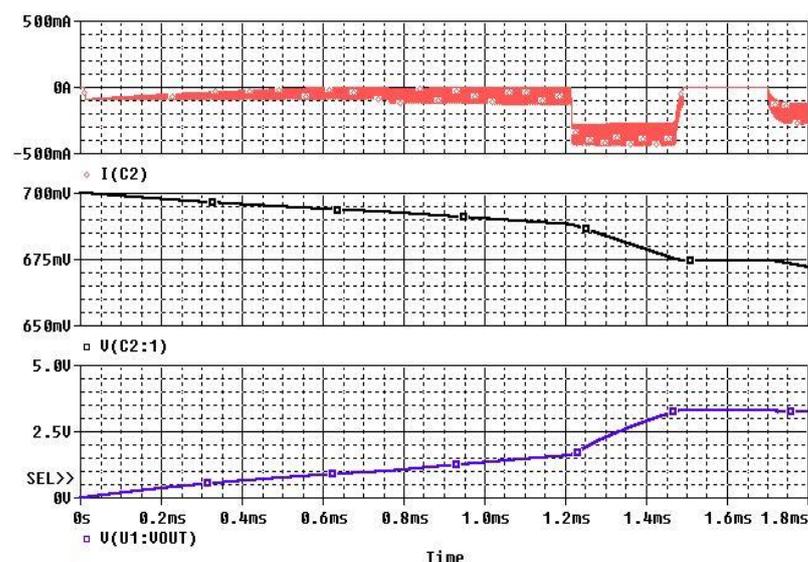
Fig 5.8: Simulation results of system with TPS61221 in Fig. 5.7

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In the following scheme a proposed feedback control loop is shown in fig. 5.9.
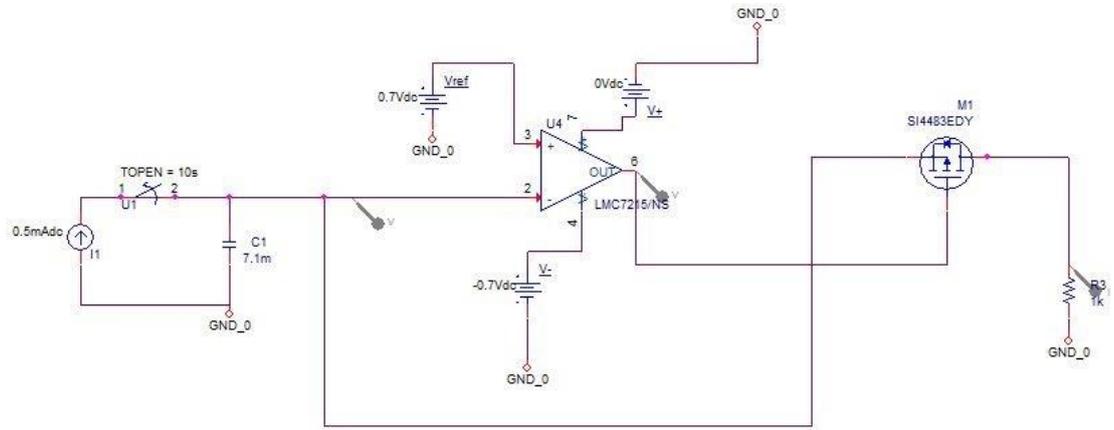
Fig 5.9: Scheme block of the feedback control loop

SI4483 *P-channel mosfet* was the transistor chosen. The Gate Thresholds Voltage are VGS(th) = -1V MIN and VGS(th) = -3V MAX. A Rail-to-Rail Comparator LMC7215/NS compared the input voltage from the cell. In the Fig. 5.10 the results of the simulation are shown, is possible to observe that after 10 s the output of the comparator switch and the current Id begins to flow.
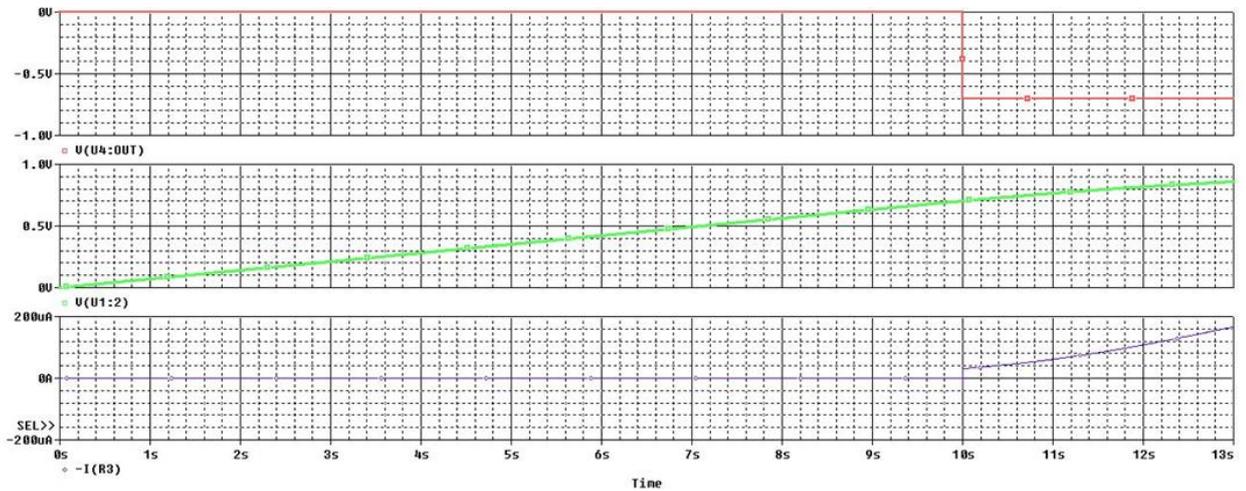
Fig. 5.10: Results of the simulation of the proposed feedback control loop

5.2.3 Energy management system with a Flyback converter

A Flyback converter was developed by N. Degrenne without external source for start-up [29] useful for power management system dedicated to MFC (Fig 5.11a). It is one of the transformer-based solutions possible to address the task of a power management system dedicated to microbial fuel cell.

The converter design was based specifically on the electrical characteristics of lab-scale WWMFCs. The circuit should start and operate at voltages lower than 0.3 V. The step-up ratio should be high to reach output voltages above 1 V. Because MFCs are strongly non-uniform generators, the converter should operate between 3 mW and 30 mW of input power with a nominal power level of 10 mW.

Efficiency has to be as high as possible. Finally, a galvanic insulation was required in order to facilitate the serial association of the outputs of the converters. Switching losses are addressed by a relatively low switching frequency (around 10 kHz), which is possible through the use of a transformer with a high primary inductance L_1 (thus a large magnetic material volume).

T_1 is a low threshold-voltage transistor that was selected as a trade-off between on-resistance and parasitic gate capacitance. The wire used for the two power windings, L_1 and L_2, are 0.56 mm external diameter and 0.20 mm external diameter for the control winding L_3. The number of turns is 10 for L_1, 20 for L_2 (1:2 ratio) and 60 for L_3 (1:6 ratio). The parameters for the coupled inductances are L_1= 277 μH and L_2 =1110 μH, R1=81 mΩ and R2 162 mΩ at 10 kHz (Fig. 5.11b).
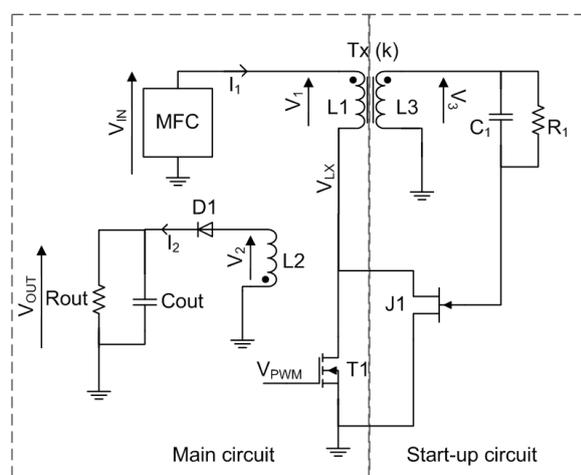
Fig. 5.11a: Simplified circuit of the flyback converter
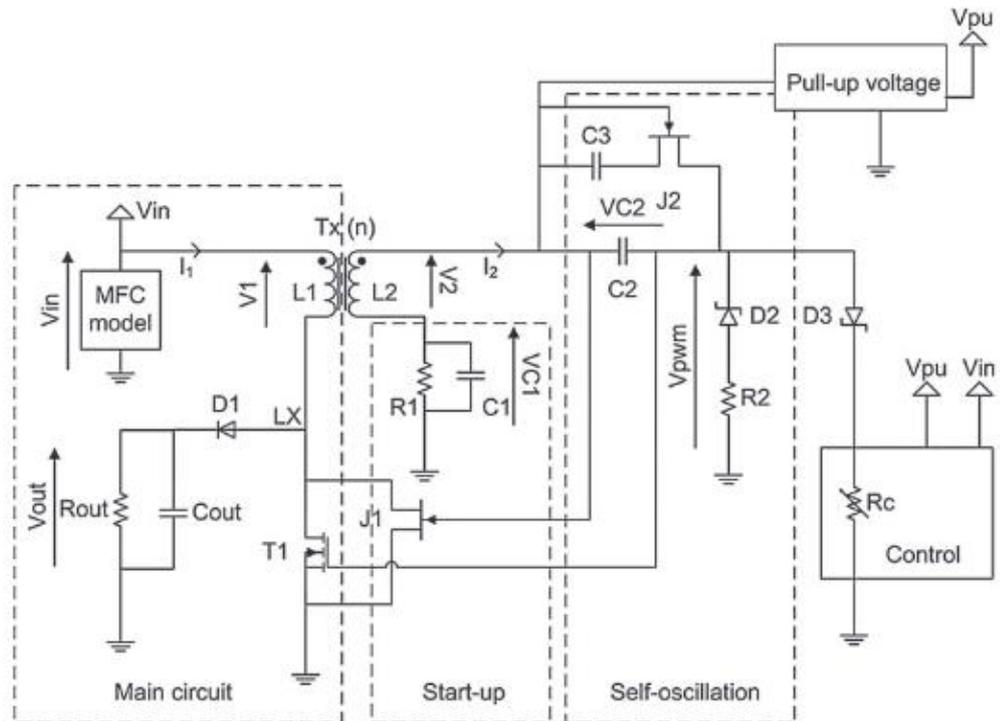
Fig. 5.11b: Schematic of the flyback converter

In 2018 the US naval warfare research program developed an underwater alert system powered by SMFCs with shared anode [5].

A power management system was designed to harvest energy from MFC (0.4 V) and transfer it directly to a 12 V lead-acid battery (3000 mAh). The battery was used to store the net charge and power the PCB as represented in Fig 5.9. This was implemented using a flyback converter as in [29, 30, 31] and functional blocks as shown in Fig. 5.12. A dual comparator block provides two BMFC voltage control operations. One channel of the dual comparator controls the voltage operating window by which the BMFC voltage is allowed to drift from 0.3 V - 0.5 V. The second channel electrically disconnects the BMFC when the voltage drops below 0.25 V.

The pulse-width modulation (PWM) block determines the frequency and duty cycle of the flyback conversion. A commercial, off-the-shelf DC/DC buck converter block provides power (μW-level) to the power management system at 2.5 V.

- Red arrow is power flow
- Blue arrow is control

Net power into battery
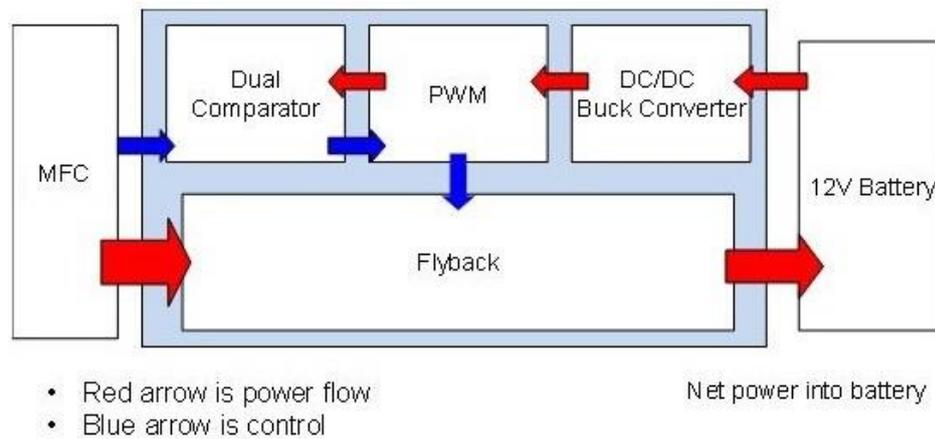
Fig 5.12: Block diagram of power management system showing power and control direction [5]

5.2.4   Long range WSN with BQ2550x series

The block diagram in Fig 5.13 shows a proposed system with BQ25505 in combination with a transceiver CC1310 and a microcontroller MSP430 to perform a WSN node with various sensors [112]. The system is based on the DC/DC boost converted by Texas Instr., which also has an integrated MPPT function. The converter harvests the energy delivered from MFC to charge a supercapacitor. Its stores the energy needed to the operation of the microcontroller and the transceiver. The sensors provide data to the RF systems that allow the node to transmit.
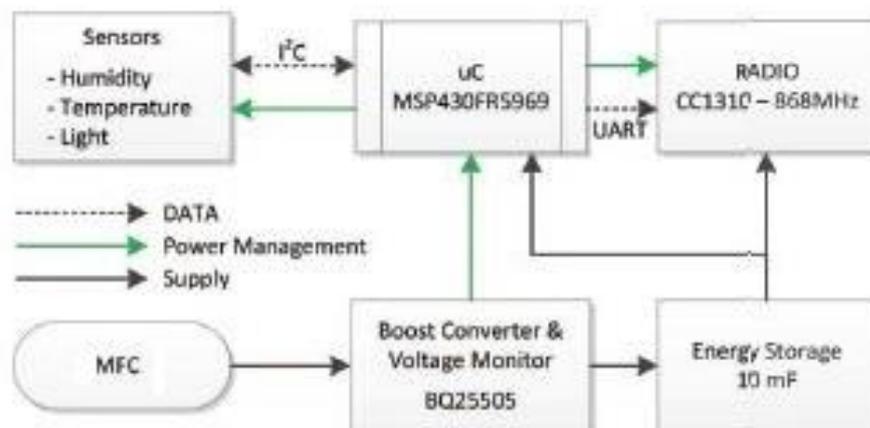
Fig 5.13: Block diagram for a long range WSN powered by MFC [112]

A system with the **BQ25504** is proposed in combination with an efficient transceiver ATA8150 by *Microchip* and the Microchip SAML21 MCU microcontroller (Fig 5.14). The transceiver ATA8150 has an RF band of 868 MHz and a *long RF range up to 10 km* in free space and tens of meters in buildings. The RF bit-rate is up to 10 kb/s, the size is 22x14 mm, and power supply range is from 2.2 to 3.6 V. It needs only 9.4 mA for data transmission. The ATA8150 is a transceiver suitable for long range WSN and low power transmission. The low power Microchip SAML21 MCU has an ARM Cortex M0+ @ 48 MHz with 256 Kbyte of flash memory and 32 Kbyte of RAM (8 Kbyte of low power RAM). The consumption is down to 35 µA/MHz in active mode and 200 nA in Sleep mode.
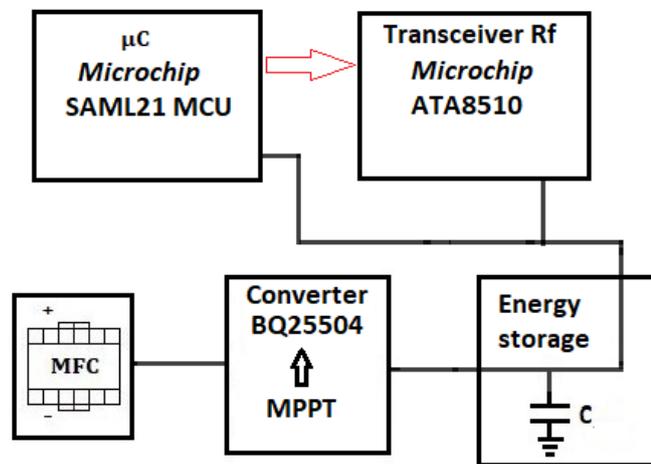
Fig 5.14: Schematic of the proposed long range WSN system

5.2.5 Voltage polarization method for energy management

A system able to exploit the advantage of the voltage polarization method on WWMFC is provided in Fig 5.15. The energy management system can be controlled and driven appropriately to appoint it. It is possible to drive the energy harvested from MFCs, usually delivered to the load, back to cell in a certain time. Moreover, the possibility of using more cells with alternating operation can support the system to provide power to the load and at the same time to self-sustain and improve electrical performance of the same cells.
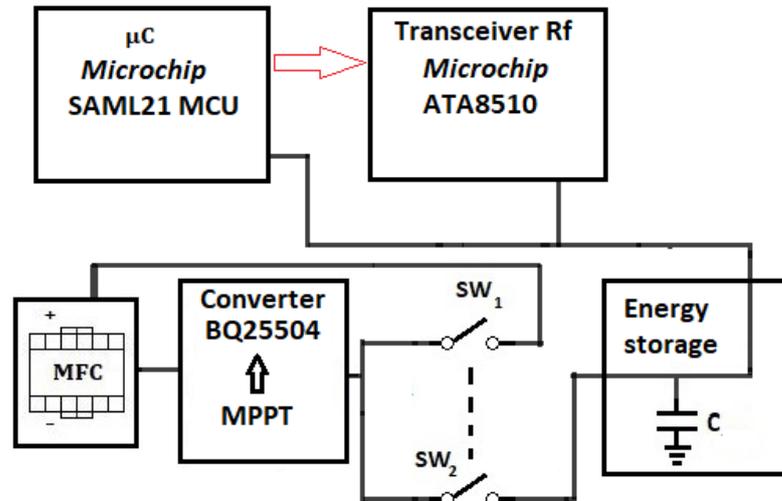
Fig 5.15: Advanced schematic of the proposed long range WSN system

5.3 Continuous power supply mode

The energy harvested from MFCs can be exploited in a continuous mode operation using more cells in alternative way. Using two cells in alternation as in [56], is possible to supply a sensor drawing power from a single cell and then giving the time to the MFC to recover from MPP operation.

The key point to address this task is the use of a capacitance between the MFC source and a DC/DC converter in the energy harvesting system and its adaptation to the system by limiting its maximum possible charge.

In Fig 5.16 is shown a proposed system with a power management unit including two capacitors and a commercial DC/DC converter to supply a temperature sensor.
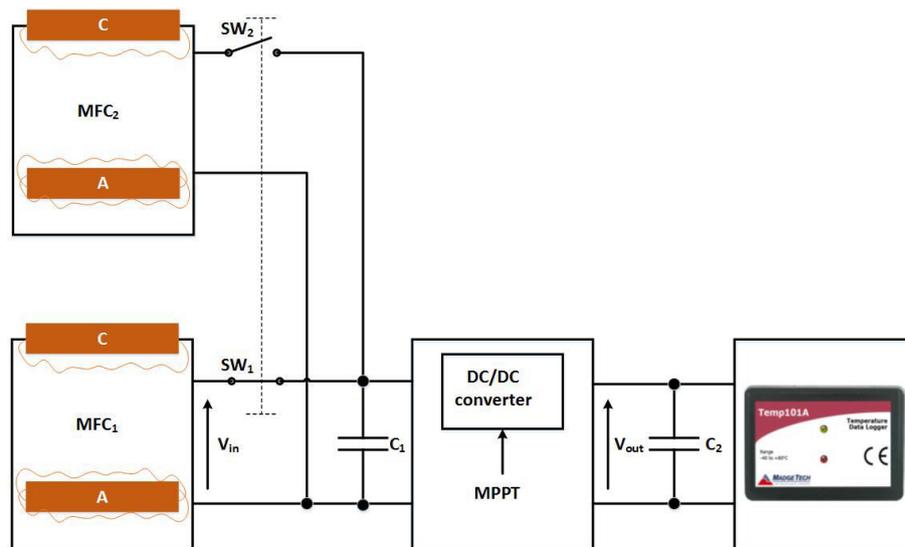
Fig. 5.16: Power management system for Continuous mode supply with 2 MFCs [56]

A continuous powering could be achieved by alternatively connect the MFCs (MFC_1 and MFC_2) as shown in Fig. 5.16. One MFC supplies the sensor while the second MFC is in the recovery mode. A power management unit with a commercially available DC/DC converter is considered to step-up the voltage and controls the operation of an MFC. Moreover, a capacitor is connected directly to the MFC to filter the output voltage fluctuation. A second capacitor at the output of the converter is needed to store the required energy for start-up of a low power device as a sensor.

The utilization of **four** cells in alternation can provide sufficient stable energy in continuous mode for more complex systems avoiding voltage decreasing issues.

Considering the DC/DC boost converter *LTC3108* by Linear Technology has the advantage to avoid the use of an external source for start-up because it works at 20mV of input. The LTC3108 by Linear is an energy harvesting interface designed for thermoelectric generator and small solar cell for wireless application and has a useful selectable V_{out} from 2.3 to 5V [140].

The start-up voltage of LTC3108 is lower than the BQ25504 by Texas, that is 80mV, but a maximum power point tracking (MPPT) is not provided.

A schematic of the basic functions of the device is reported in Fig. 5.17. The LTC3108 uses a step-up transformer with a turn ratio of 1:100 and a MOSFET to form a resonant oscillator able to operate from very low input voltages. The value of the supercapacitor C_{in} is 1 F. The capacitor C_{out} has a value of 470 µF and C_{store} is equal to 1 mF. The capacitor C_3 has a value of 1 µF and the value of C_4 is 2.2 µF. The transformer secondary winding voltage is boosted and rectified using capacitors C_1 and C_2: they have respectively a value of 1 nF and 1 pF.

Working on the electrical charge given to a capacitor by a cell is possible to assure a continuous mode operation. It is possible to limit the charge of a capacitor taken from MFC in a primary stage before DC/DC converter such as up to 50 mV, in this way every switch time a cell will be not heavy discharged and after loading, it can be restored in a sleeping mode when another cell is working.

Fig 5.17: Proposed energy management system with low start-up LTC3108

When the switch SW opens, a super capacitor of 1 F is isolated from the circuit and the MFC is directly connected with the super capacitor. During discharging, the switch SW is closed, and the supercapacitor is connected to the boost converter which uses the charge accumulated so far.

The charging time of a supercapacitor is influenced by the energy generation of MFC, the capacitance value, the characteristics of the DC-DC boost converter and the connected load.

The maximum charging voltage can be chosen to be 50 mV and the minimum voltage to which the supercapacitor can be discharged can be selected as 20 mV, considering that the proposed boost converter operates down to 20mV. The maximum can be put to 50 mV because it is the minimum voltage required to obtain continuous power output by the DC-DC boost converter.

The charging and discharging voltage values can simply be adjusted to fit the converter and supercapacitor.

Limiting the discharging and charging voltage of the supercapacitor (20mV to 50 mV) is the requirement for continuous power produced by the energy management system with four MFCs in alternation as sources (Fig. 5.18). In this way it is possible to supply low power devices in a continuous power supply mode without require freezing repetitively the WSN node.
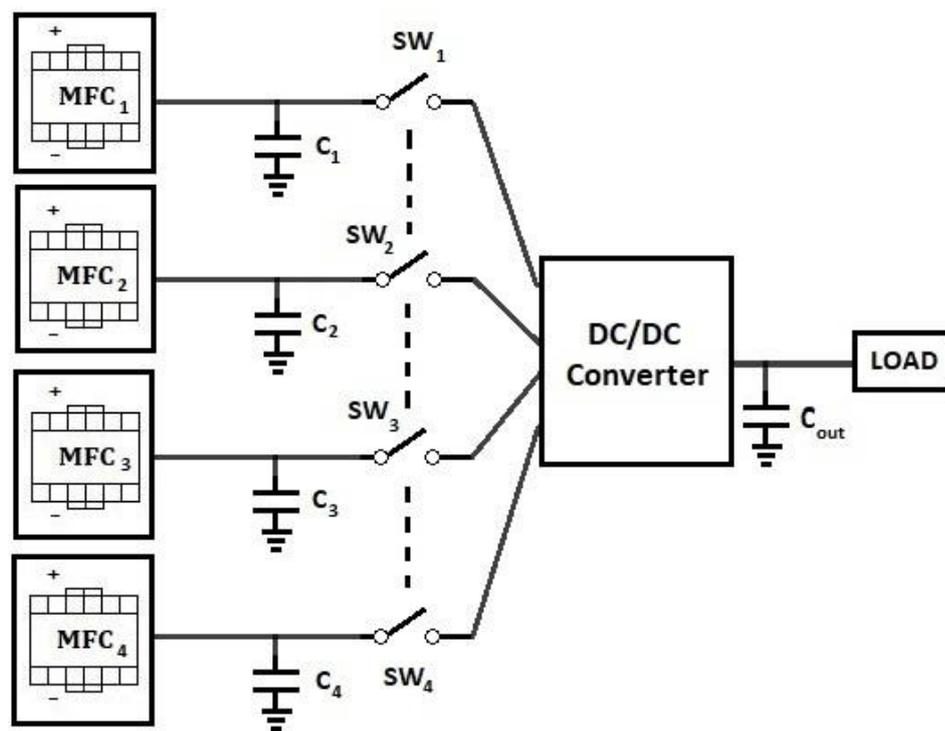
Fig.: 5.18: Schematic of the proposed system with 4 MFCs

Each of the four switching is timed, the timing allows to operate only one cell at a time. Every 1.5 minutes one switch is closed, allowing to supply the DC/DC converter and all the other one is closed. So, at the beginning of a time of 1.5 minutes the SW_1 will be closed, while all other switches are open, at the end of the 1.5 minutes the SW_1 will be open and the next SW_2 will be closed, and so on for all other switches. Each supercapacitor voltage is charged up to 50 mV at the beginning of this time to arrive at the end of the 1.5 minutes to 20mV. At this time the corresponding switch will be open and the next one will be closed, enabling the corresponding supercapacitor to decrease again its voltage from 50mV to 20mV supplying the converter until the switch will be open.

6. Conclusions and future development

Microbial fuel cell is a rising energy harvesting technology that can be used to supply low power devices for many purposes and applications or directly as biosensor. As a matter of fact, it is now a platform technology due to its effectively multiple possible applications.

The application fields of MFCs can vary from bioremediation and energy recovering in urban waste-water treatment plants to precision farming monitoring. The possibilities to use MFCs in different environments open other way to exploit the energy recovery and bioremediations abilities, as well as the use as biosensors. From open sea to harsh environments the reactors can be properly configured case by case using Benthic or Waste water or Terrestrial microbial fuel cells. Furthermore, the MFC energy harvesting technique can be considered as the only technology to recover electricity from waste without the addiction of an external source.

The contributions to the dissemination of MFCs are the following.

In chapter 2 the context of biofuel cell is introduced and the basic principles of operation and the main application of MFCs are explained. In the chapter are listed the numerous parameters that define the MFC in all its aspects. A perspective is to tune these parameters for maximizing the production of electricity. The survey includes an evaluation of the impact of different electrode materials, substrate used, and bacteria involved in the chemical process. Also, the specific design of lab-scale MFCs is presented. Two different lab-scale MFCs typologies were built: TMFCs and WWMFCs. Moreover, the two mode of use of WWMFCs as continuous flow or batch mode was examined. At the end of the chapter, the main issues regarding MFCs functioning and testing are inspected.

In Chapter 3 a proper measurement system designed specifically for tests on MFCs is presented. It is able to assure an accurate measure of any electrical values and parameters needed for the electrical characterization of reactors in single configuration or in multiple connection.

The Chapter 4 includes all I/V experimental results done on MFCs. Tests were performed on lab scale version of WWMFCs and TMFCs. The solutions used to feed WWMFCs were different and in some cases was used real waste water, in others proper synthetized solutions were made on purpose. The methods for synthesizing the solutions is described. The influence of the main parameters as pH and temperature was analysed for both type of cells. The experimental campaign includes measurements of reactor in single configuration or arranged in pack in series or parallel connections.

Chapter 5 contains a survey on the possible application of MFCs in many fields. It is described the possible solutions for energy management systems able to exploit the energy delivered by MFCs to supply ultra-low power devices, like those used for a node of a WSN. Also, it is present a comparison between the most recent low power devices required to build a WSN. Many different systems are proposed according to the types of reactors used and the exploitation of the energy provided by the cells in a timed or continuous supply mode.

6.1 Perspectives

Considering the advances in the fields of fluid dynamics and nanotechnology in recent and next years, the combination of these disciplines will could open new frontiers in electronics in the future, when components and wires will be made using the property of water as conductor in place of materials as copper for wires and cables, overcoming also the great issues of dispersion due to the joule effect. Then, bioelectricity from BESs will be able to supply most of the devices.

Efforts are needed to improve the energy conversion in microbial fuel cells with various set ups, operations, electrode and membrane materials, substrates and microorganisms. As a matter of fact, main issues are related to the fact that MFCs produce a wide range of performance in different configurations and measurement setup, a large database of MFC behaviour is needed, especially about the MFC kinetics and sampling time. As future development, the results about electrical behaviour of MFCs will be compared with tests of in different conditions or reactors configurations.

For the terrestrial microbial fuel cell, a large work of classification is needed for all existing soil types in different boundary condition with respect to the electrical behaviour of the reactor filled with the soils. This classification is useful to exploit the use as biosensor of TMFC and also to find best way to improve energy conversion rate. For waste water microbial fuel cell, a different issues with respect of TMFC is the batch or continuous flow mode, the batch mode is more suitable for bioremediation instead a continuous flow is more suitable for energy recovery or the use as biosensor.

Properly designed measurement systems are necessary to test MFCs, as the one presented in this thesis. Contrarywise, the tests can suffer of many issues from the accuracy of the measurement time to the appropriate collection of data. In case of large stack of MFCs, the measuring system has to be improved to assure the accuracy to test high level of energy, especially for voltage measurement for large number of connections in series.

The connection of a big number of MFCs as a cluster suffers from issues directly related to the number of MFCs. More is the number of MFCs more is needed a reduction of the space occupied by the cell and in particular is needed to reduce the distance between the reactors to minimize the length of connecting wires and avoid losses.

The collaboration among Laboratoire Ampère of University of Lyon and DIET department of University of Rome has allowed the sharing of knowledge and expertise on MFC technology.

The multidisciplinary nature of the research makes it particularly stimulating and interesting, combined with the importance and vastness of the topics covered: from microbiology to chemistry and engineering.

Strengthening international cooperation on sustainable urbanisation is one of the most futuristic topics for European Union as indeed are sustainable energy recovery systems and bioremediation systems.

7. APPENDIX

7.1 Appendix A – Bibliography

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7.2 Appendix B – Board components

7.2.1 Hardware Description

In the following paragraphs a description of the hardware characteristic of the measuring board (Fig 7.1) is provided with project design feature and block schemes. A PCB layout of the board is shown in Fig. 7.2.
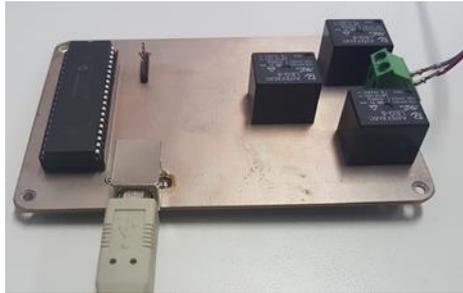

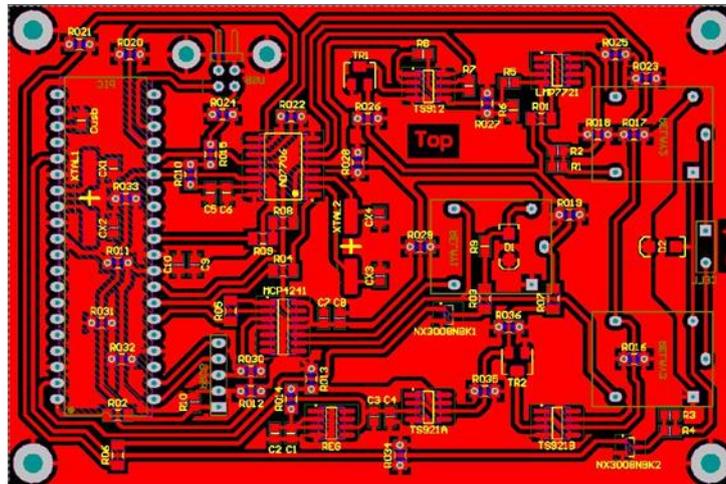*Fig. 7.1: Photo of the measuring board dedicated to MFC with connections*

Fig. 7.2: Measuring Board PCB layout

7.2.2 Relays and accurate voltage reference

The relays chosen for the project were LEG-5 relays by RAYEX ELEC (Fig. 7.3). The LEG-5 is an electromagnetic relay with SPDT configuration (Fig. 7.4) and rated coil voltage of 5V. The operating temperature is from -25°C to 80°C and the operate and release time is 8 ms. When pin 3 is connected to pin 5 the condition is switched OFF or in case of pin 3 connected to pin 2 the condition is switched ON.

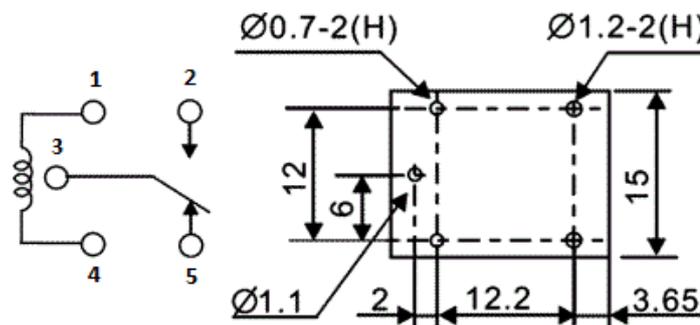*Fig. 7.3: Image of a LEG-5 RELAY by RAYEX ELEC*

Fig. 7.4: Output configuration of a LEG-5 RELAYS by RAYEX ELEC

The **REF192** is a 2.5V precision voltage reference with Short-Circuit Protection. It is a precision band gap voltage reference that uses a patented temperature drift curvature correction circuit and laser trimming of highly stable, thin-film resistors to achieve a very low temperature coefficient and high initial accuracy. The REF192 series is made up of micropower, low dropout voltage (LDV) devices, providing stable output voltage from supplies as low as 100 mV above the output voltage and consuming less than 45 μA of supply current. The REF192 series are specified over the extended industrial temperature range (−40°C to +85°C).

The REF 192 used for the project had a SOIC_8 package (Fig. 7.5), Small Outline Integrated Circuit (SOIC) is a surface-mounted integrated circuit (IC) package.
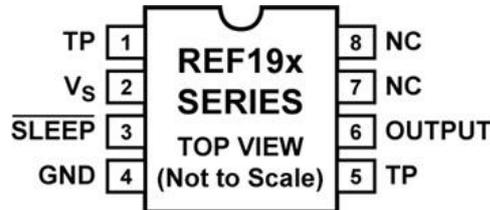
Fig. 7.5: REF192 Lead standard small outline package SOIC_8 Pin Configuration

The **TS921** device is a rail-to-rail single BiCMOS operational amplifier optimized and fully specified for 3 V and 5 V operation. Its high output current allows low load impedances to be driven (80 mA able to drive 32 Ω loads). The TS921 device exhibits very low noise 9 (nV/√ Hz), low distortion and low offset. It is fully specified for instrumentation with low noise as key factor. The V_{CC} supply voltage operates from 2.7 to 12 V and the operating free air temperature range is from -40°C to +125 °C.

The package of the operational amplifier TS921 used for the project of the measuring instrument was SOIC_8 (Fig. 7.6).
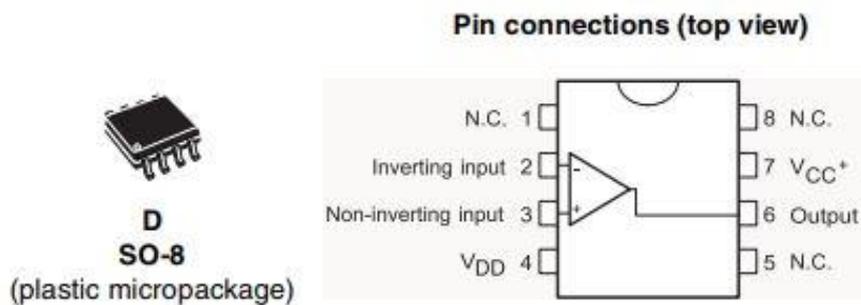

Fig. 7.6: TS921 SOIC_8 package and pin configuration

7.2.3 Microcontroller and ADC (Analog to digital converter)

The microcontroller chosen was a **PIC18F4550** by Microchip. PIC (Programmable Intelligent Computer) is a family of microcontrollers made by Microchip Technology (Fig. 7.7).

The PIC18F4550 is ideal for low power applications, for embedded control and monitoring applications that require periodic connection with a personal computer via USB for data upload/download and firmware updates. The program memory type is Flash, and the size is 32Kb. It has SDRAM of 2048 byte. The operating voltage range is from 2V to 5.5V and the operating temperature is from -40°C to 85°C.

The PIC18F4550 operation is supplied via the USB PORT of Vcc=+5V from the computer connection. The package used is a 40-Pin PDIP.
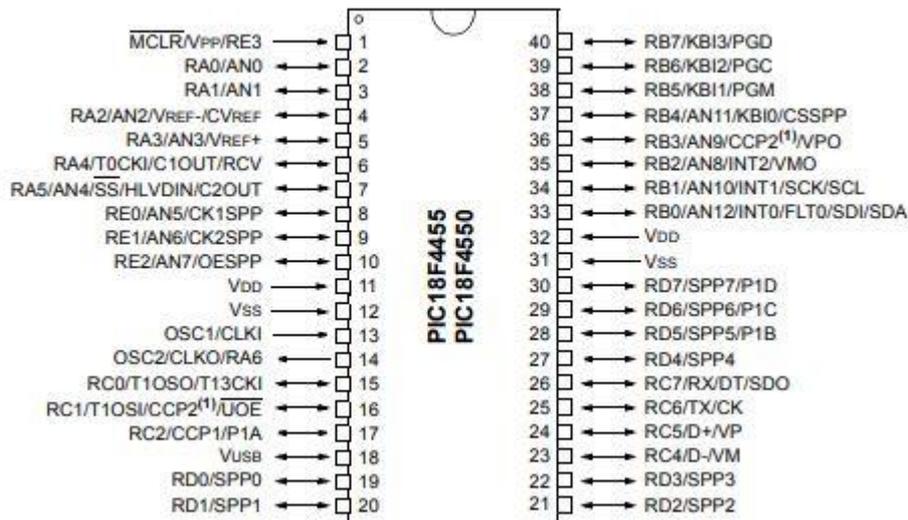
Fig. 7.7: Pin configurations of PIC18F4550 40-pin PDIP package

The PIC18F4550 has an integrated 10bit ADC, in place of this it was preferable to use a low noise ADC to get more accurate measurements, the AD7706 16bit Sigma-Delta ADC by Analog Devices (Fig. 7.8).

The **AD7706** is a 16bit Σ-Δ analog-to-digital converter (ADC) with on-chip digital filtering, intended for the measurement of wide, dynamic range, low frequency signals. Each contains a Σ-Δ (or charge-balancing) ADC, a calibration

microcontroller with on-chip static RAM, a clock oscillator, a digital filter, and a bidirectional serial communication port.

The parts consume only 320 µA of power supply current, making them ideal for battery-powered or loop-powered instruments. These parts operate with a supply voltage of 2.7 V to 3.3 V or 4.75 V to 5.25 V.

The AD7706 is complete analogic front ends for low frequency measurement applications. The AD7706 features three pseudo differential input channels. This 3-channel device can accept low level input signals directly from a transducer and produce serial digital output. The devices employ a Σ-Δ conversion technique to realize up to 16 bits of no missing codes performance. Also, it has the ability to buffer the analogic Input.

In the measurer instrument project, the AD7706 is supplied from the USB port with Vcc=+5V
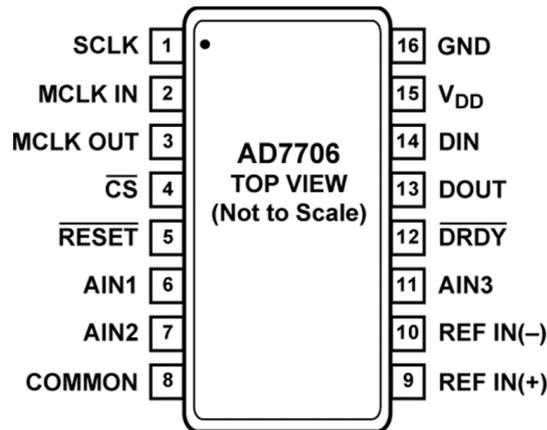
Fig. 7.8: AD7706 pin configurations

Furthermore, another component used was a **MCP4241** 10kΩ Digital potentiometer by Microchip (Fig. 7.7), it permits to switch load value in the *power analysis phase* for measurements of cells power performance. The MCP4241 devices are non-volatile, 7-bit (129 wiper steps) digital potentiometers with EEPROM and an SPI compatible interface. The operating temperature range is from -40°C to +125°C, and operating voltage from 2.7V to 5.5V. Low-Power Operation: 1µA Max Static Current.

Fig. 7.9: MCP4241 Package and PIN configurations

A 1-814-258-31 Sony **Quartz Crystal Oscillator** was insert in the project to provide the clock to the system. It delivers the clock signals XTAL1 of 20 MHz to the PIC and the XTAL2 4.9512 MHz to the ADC AD7706.
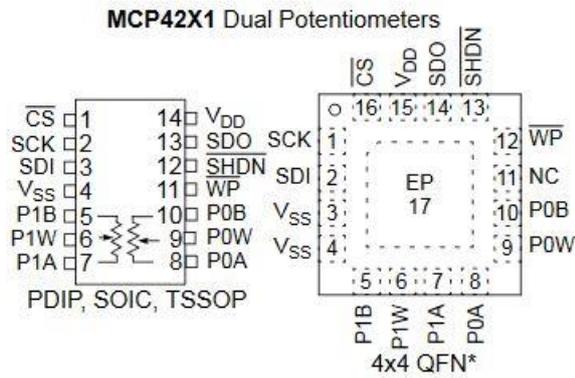
The bills of materials in fig. 7.10 is referred to the schematic project of the measurer board in the Fig 3.3 developed with the program Altium.

Footprint	Comment	LibRef	Designator
WSOIC16	AD7706	AD7706	AD7706
0805	10u	Cap	C1, C5, C7, C9
0805	100n	Cap	C2, C4, C6, C8, C10
0805	1u tant	Cap	C3
2DIP-200	- +	HEADER2	CELL
0805	330nF	Cap	Cusb
0805	18pF	Cap	CX1, CX2, CX3, CX4
SMB_SD	S-Diode	S-Diode	D1, D2
SOIC8	LMP7721	LMP7721	LMP7721
SOIC14	10k	MCP4241	MCP4241
SOT23-3	DMN3404	DMN3404	NX3008NBK1, NX3008NBK2
PDIP600-P40	PIC18F4550-I/P	PIC18F4550-I/P	PIC
HDR1X5	Header 5	Header 5	PROG
1206	0	Res	R01, R02, R03, R04, R05, R06, R07, R08, R11, R22, R5, R6, R7, R8
0805	100	Res	R1, R2, R5, R6, R7, R8
0805	18	Res	R3, R4, R9
0805	1k	Res	R10
SOIC8	REF192	REF192	REG
REL5	RELAY	LEG-5	RELAY1, RELAY2, RELAY3
3224W	10k	TR	TR1, TR2
SOIC8	TS912	TS912	TS912
SOIC8	TS921	TS921	TS921A, TS921B
USB_B	USB_B	USB_B	USB
SMD_XTAL	20MHz	XTAL	XTAL1
SMD_XTAL	4.9152MHz	XTAL	XTAL2

Fig. 7.10: Bills of materials of the measurer board project

7.3 Appendix C – Publications List

7.3.1 List of Articles and Publications

Journals:

- Pietrelli, A., Micangeli, A., Ferrara, V., Raffi, A. (2014). Wireless sensor network powered by a terrestrial microbial fuel cell as a sustainable land monitoring energy system. *Sustainability*, *6*(10),7263-7275.

- Ferrara, V., Pietrelli, A., Chicarella, S., Pajewski, L. (2018). GPR/GPS/IMU system as buried objects locator. *Measurement*, *114*, 534-541.

Proceedings:

- Pietrelli, A., Ferrara, V., Micangeli, A., & Uribe, L. (2015, February). Efficient energy harvesting for microbial fuel cell dedicated to wireless sensor network. In *AISEM Annual Conference, 2015 XVIII* IEEE.

- Pietrelli, A., Ferrara, V., Khaled, F., Allard, B., Buret, F., Costantini, F. (2016, June). Electrical characterization of MFC for low power applications. In *Environment and Electrical Engineering (EEEIC), 2016 IEEE 16th International Conference on* (pp. 1-5). IEEE.

- Pietrelli, A., Ferrara, V., Allard, B., Buret, F., Costantini, F., Lovecchio, N. Khaled F., (2017)."Microbial Fuel Cells: Performance and Applications." *World Academy of Science, Engineering and Technology, International Journal of Energy and Power Engineering*.

- Pietrelli, A., Allard, B., Ferrara, F., Buret, F., (2018) "Electrical valorisation of Microbial fuel cell", *proceedings of Symposium de Genie Electrique SGE 2018, Nancy*.

- Pietrelli, A., Ferrara, V., Allard B., Buret, F., Khaled, F., Bavasso, I., Costantini F., 'MFC Performance and Applications,' poster presentation at *SIE 2017, 49th Annual Meeting of the Associazione Società Italiana di Elettronica*, Palermo, 2017.

- Pietrelli, A., Chicarella, S., Ferrara V., (2015) 'Integration of Ground Penetrating Radar with Global Position System and Inertial Measurement Unit for archaeological application', *proceedings of 1st International Conference Metrology for Archaeology*, 1,112-115.

- Chizh M., Pietrelli A., Ferrara V., Zhuravlev A., 'Development of embedded and user-side software for interactive setup of a frequency-modulated continuous wave ground penetrating radar dedicated to educational purpose,' *Microwaves, Antennas, Communications and Electronic Systems (COMCAS), 2017 IEEE International Conference on*, pp. 1-5.

- Pietrelli, V. Ferrara, B. Allard, F. Buret, N. Lovecchio, 'An original measuring board for MFC electrical characterization,' poster presentation at *SIE 2018 50th Annual Meeting of the Associazione Società Italiana di Elettronica*, Naples, 2018.

- Pietrelli A., Ferrara V., Allard B., Buret F., Lovecchio N., Bavasso I., 'Custom measuring instrument dedicated to microbial fuel cell characterization,' poster presentation at *EU-ISMET 4 2018, International Society for Microbial Electrochemistry and Technology European edition*, 12th-14th September, Newcastle, UK, 2018.

- Ferrara V., Pietrelli A., Chizh M., Mazzetta M., 'Radar onda continua modulata in frequenza (FMCW) a uso educazionale: rilevatore di distanza e velocità, applicazioni Ground Penetrating Radar,' poster presentation at *Maker Faire 2017 Europian edition 4.0*, Rome, Italy, 2017.

7.3.2 Conferences, Symposia and PhD school attended:

- AISEM Conference XVIII, *sensors and microsystems*, February 2015, Trento.

- PhD Training school: *Applications of Ground Penetrating Radar in Urban Areas*- the Sensitive Case of Historical Cities, May 2015, Cracow University of Technology, Poland

- 1st International Conference on Metrology for Archaeology, October 2015, Benevento, Italy

- ApplePies international conference - Applications in Electronics Pervading Industry, Environment and Society, May 2016, Rome, Italy

- EU-ISMET 3, *International Society for Microbial Electrochemistry and Technology European edition*, 26th-28th September 2016, Rome , Italy

- EXPERIMENTA 2016, Minatec, Scientific Forum, MFC stand, October 2016. Grenoble, France

- 15th *International Conference on Environment and Electrical Engineering* (EEEIC), October 2016, Florence, Italy

- *SIE 2017 (49th Annual Meeting of the Associazione Società Italiana di Elettronica)*, annual conference + PhD school, June 2017, Palermo, Italy

- Final Conference *EU COST Action TU1208*: September 2017 Warsaw, Poland

- Evobliss *Triple Autumn PhD School*, IUT University of Copenhagen, September 2017, Copenhagen, Denmark

- *ICFCET 2017 : 19th International Conference on Fuel Cell Engineering and Technology on* November 2017, London, United Kingdom.

- *Maker Faire* - European Edition 4.0, Roma, December 2017, Italy

- *SIE 2018 (50th Annual Meeting of the Associazione Società Italiana di Elettronica) Napoli*, annual conference, June 2018, Napoli, Italy

- *SGE 2018, Symposium de Génie Electrique,* July 2018 Nancy, France

- *EU-ISMET 4 2018, International Society for Microbial Electrochemistry and Technology European edition*, 12th-14th September, Newcastle, UK

7.4 Appendix D – Joint-supervision PhD

7.4.1 PhD organization, future development and European collaboration

The PhD program in joint supervision has the objective to create a wide net on the microbial fuel cell research, considering that right now there is an extensive interest in each European country regarding this research. The collaboration is focused on improving the knowledge and the training about Microbial fuel cell research. Starting from the countries involved in the joint supervision PhD program that has been activated, the purpose is to enlarge the net to other country to spread the research more is possible.

The partner involved in the joint-supervision PhD program was the Department of information engineering, electronics and communications (DIET) of Sapienza University of Rome for Italy, and Laboratoire Ampère (INSA-ECL), Université de Lyon for France.

A proposal for a European Horizon 2020 project is currently in preparation with MFCs as nature-based solution for rehabilitation of urban and rural ecosystems and electricity recovery.

7.4.2 Prizes, projects and awards

In the last four years the project around the PhD program in joint supervision on Microbial Fuel Cell between Laboratoire Ampère at Ecole Centrale de Lyon and DIET department at Sapienza University of Rome has harvested a total amount of financial support of around 28.000 euro from 4 different calls for research grant:

- An amount of 12.000 euro was raise in 2015 from the "Torno Subito" call for grant of Lazio region. This call funded by European community was concerned the support to young citizens with a degree and born in Lazio region, that intended to spend a period abroad. Partnership was done with Ampère Lab of Université de Lyon and DIET department of Sapienza University of Rome.

- A grant of 1.000 euro for equipment, instrumentation and dissemination of research was gained from a call for grant Starting Research Funding University Projects for young researchers of Sapienza University of Rome in the context of Scientific Research Year 2016.

- A sum of 9.000 euro has come from Sapienza University in the framework of funds for international cooperation in research funded by Italian government. I won in 2016 a call for grant that was open for PhD student in partnership with a foreign institution (Ampère Lab - École Centrale de Lyon)

- A support for PhD mobility was gained from the IDEXLYON call for grant in 2018. The amount of financing granted was 6.000 euro for incoming mobility grant of IDEXLYON 2018 from Rhone des Alpes region in collaboration with Université de Lyon.

In the context of Scientific Research Year 2015, I have won a research contract of 1 year of a gross amount of 24.000 euro from the budget of a Medium Funding University Projects of Sapienza University on: Design and construction of an FMCW GPR radar system (continuous wave modulated in frequency Ground Penetrating Radar), compatible with transport by UAV (Unmanned Aerial Vehicle), for localization and rescue applications of people buried by snow or debris, in emergency scenario. During the project I was able to improve my skills and experiences on topics regarding ground penetrating radar systems.