An investigation on polymer ion exchange membranes used as separators in microbial fuel cells

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Abstract

An ion exchange membrane is a polymer matrix of cross linked polyvinyl chloride macromolecular chains, on which are grafted ionic functional sites. The cation exchange membrane (Nafion) and the anion exchange membrane (AMX) were used as separators in Microbial Fuel Cells (MFC). In effect, the MFC with the anion membrane AMX, gave relatively higher power density (1.10 mW/m2) compared to the cation exchange membrane Nafion (0.45 mW/m2). Really, with the AMX separator, the metal ions present in the wastewater anolyte compartment, were blocked by the membrane giving way to the protons to displace freely and be reduced efficiently at the cathode. Whilst in the mono-compartment cell, the ions moved sideways between anode and cathode, yielding the highest power density (11.90 mW/m2) so far obtained.

Keywords: **Polymer membranes ; Wastewater ; Microbial Fuel Cell; Nafion; AMX.**

I. Introduction

Polymer ion exchange membranes are now largely used as separators in electrodialysis and fuel cells because they allow selective ion transport between anolyte and catholyte. The presence of a miscible solvent modifies the transport properties of the membrane. In effect, the mobility of protons through the cation exchange membrane (CMX) decreases strongly with the presence of the solvent inside the membrane, while that of the metal remains unaffected [1]. Moreover, the increase of organic acid solubility was also successfully achieved using ion exchange membranes in hydro-organic media [2]. Besides, in order to increase its proton conduction against metal ions, the cation exchange membrane Nafion 117 has been modified chemically using the conducting polymer pyrrol along with the suitable oxidant FeCl3[3]. The modified membrane has a high ionic conductivity and a low electrical resistance, so very convenient in Hydrogen and Direct Methanol Fuel Cells, for producing clean energy and preserving environment from pollution [4, 5]. Besides, the partially fluorinated membrane such as Nafion with high degree of sulfonation exhibits better oxidative stability. The membrane presents good proton conductivity, good thermal and hydrolytic stabilities [6]. Moreover, the physico-chemical properties of the novel sulfonated poly (glycidyl methacrylate) grafted Nafion membranes prove their potential application in fuel cells. The results showed that the modified membranes have high water uptake, no impact effect on the stability of its dimensions in methanol, high thermal stability and a decrease of methanol permeability with increasing polymer content. [7]. In addition, poly(dimethyl benzimidazolium) carbonate membranes, showed high water uptake as well as ion conductivity and therefore can be good candidate for anion exchange membrane fuel cells [8]. The ion competition through the Nafion 117 proton exchange membrane has been investigated and showed a ratio of permelectivity between protons and metal ions [9]. On an energetic scale, in order to face lack of affordable energy and pollution, it is primordial to develop new and sustainable alternatives generated upon the conversion of sustainable biomass. Research has been now focusing on the microbial fuel cells (MFCs) to address the development of new energy sources from biomass [10].

Bioreactors based on power generation in MFCs represent a completely new approach to wastewater treatment. It was demonstrated that it is possible to produce electricity in a MFC from domestic wastewater, while at the same time accomplishing biological wastewater treatment [11]. These systems could be used in biomass-based energy production, but many technical challenges must be overcome before they will be practical for renewable energy production [12]. MFCs function on different carbohydrates including acetate, lactate, and glucose, but also on complex substrates present in wastewaters. Depending on the operational parameters of the MFC, different metabolic pathways are used by the bacteria. This determines the selection and performance of specific organisms [11, 13]. It was demonstrated that a significant improvement can be expected by increasing microbial settlement on the electrode surface [14]. Also, temperature was found to have impact on electrodes potentials to generate electricity using brewery wastewater [15].

Much research on MFCs experiments is under way with great potential to become an alternative to produce clean energy industry in the future from renewable waste [16]. In view of all this interesting bibliography, we investigate in the present work, the performances of MFCs using the cation exchange membrane Nafion and the anion exchange membrane AMX were compared between each other. Their energy efficiencies were therefore tested against one-compartment fuel cell.

II. Materials and Methods

A. Materials.

The ion exchange membranes Nafion® 117 membrane from DuPont de Nemours (USA), CMX and AMX Neosepta from Tokuyama Soda (Japan) were used for the transport of metal cations and protons and applied as separators in MFC. Their physico-chemical characteristics are given in table 1.

The sludge was taken from a car washing station in Oran (Algeria). The reagents hydrochloric acid, sodium hydroxide and glucose anhydrous were purchased from Biochem Chemopharma, Sigma-Aldrich and Biochem Chemopharma respectively. The materials used for the electrodes were CF (bio-anode) and the alloy platinum-titanium grids (cathode) purchased from Baoji Qixin Titanium Co., Ltd. The multi-meters Fluck 175 were used for measurements of voltage and current. The pH meter Hanna was used to adjust the pH of solution. The Phywe 13701.93 conductivity meter was used to measure the leachate (wastewater) conductivity.

The solutions were all prepared using distilled water. The potentiostat-galvanostat Voltalab PGZ301 was also used for electrochemical characterization using cyclic voltammetry and impedance spectroscopy techniques. The copper analysis was carried out using atomic absorption spectroscopy using PinAAcle 900H PerkinElmer.

Tab.1 Ion exchange membrane characteristics [17, 18, 19, 20].

Characteristics	Nafion-117	CMX	AMX
Functional group	-SO3-	-SO3-	NR3+
Ion exchange capacity (meq/g)	0.9	1.5 – 1.8	1.4 – 1.7
Transport number	≈0.99	>0.98	-SO3-
Thickness (µm)	183	140 – 200	120 – 180
Electric resistance (Ω.cm-2)	1.5	2.0 – 3.5	2.0 – 3.5
Water content (%)	16	25 - 30	– 30

B. Methods

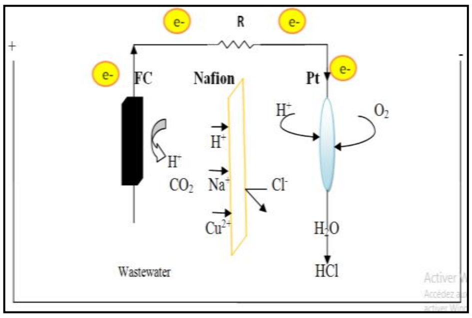
Preparation of microbial inoculum

The wastewater microbial inoculum was prepared by mixing 200 g of the sludge taken from a washing station located in Oran (Algeria),with 1 L of distilled water. The mixture was placed in an Erlenmeyer flask and stirred with a magnetic stirrer during 24 hours. Then, it was filtered with a filter paper to give the leachate medium having an ionic conductivity of 1.92 mS / cm and a pH 8.2.

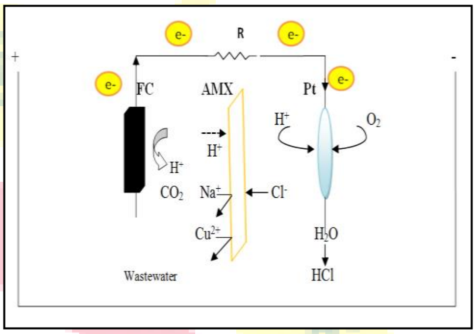
MFC designs

As illustrated by Figs.1a and 1b the MFC consisted of two half-glass cell, connected to each other by the Nafion® membrane (cationic exchange perfluorinated membrane)and AMX membrane (anionic exchange perfluorinated membrane) respectively. The CF (1.0 x1.2x4.0 cm) bio-anode and the platinized titanium sheet (1.0 x 5.0 cm) were placed inside the anolyte and the catholyte respectively. The anolyte contained the leachate solution, whereas the catholyte only hydrochloric acid solution (10-3mol/l). The solutions were stirred with magnetic bars. The top end of the anolyte was tightly sealed with paraffin film to avoid penetration of oxygen. The circuit of the cell was closed with an external resistance of 1 000 Ω. Besides, the mono-compartment fuel cell is simply illustrated by Fig.1c. The cell voltage was measured with a multimeter placed in parallel. Owing to the fact of very low values, the current density was deduced using Ohm's law. After 5 days of functioning, both the level of the solution and the current density fell down, as a result of the decrease of the contact surface of interface solution/bio-anode. So, the amount of leachate removed, was substituted by the same amount of glucose (0.1 mol/l). Owing to acclimation, a significant increase of the current was observed after 5 hours and was approximately twice higher than that obtained with just pure leachate. Then, it continued to increase provided the fuel was added conveniently.

Moreover, as the MFC became mature, the current was high and stable. The power density was therefore determined in terms of current density by varying the external resistance from 10 MΩ down to100 Ω. Generally, the value of the current stabilized within 3 minutes. However, the required time needed to reach the initial value, depended upon the value of the resistance. In effect, the smaller is the value of the resistance, the higher is the cell discharge [21].



(a)



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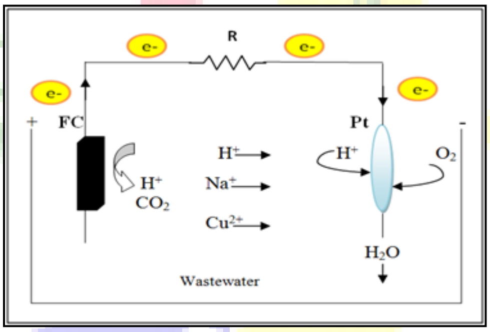


(c)

Fig.1 Schemes of different microbial fuel cell: (a) with Nafion membrane; (b) with AMX membrane and (c) mono-compartment cell

Electrochemical characterization

Anode characterization was evaluated with cyclic voltammetry conducted by a potentiostat galvanostat Voltalab PGZ301 in a three electrode setup electrochemical cell. A Pt plate was used as a counter electrode (anode), Ag/AgCl used as reference electrode and FC used as working electrode. Cyclic voltammetry was carried out using the potential range 1.0 to -1.0 V at scan rates 5, 10, 20, 50 and 100 mV/s. Electrochemical impedance spectroscopy (EIS) was also carried out in the frequency range100 KHz - 100 mHz.

III. Results and Discussion

A. *Evolution of Electro-Motive Force (EMF) of Nafion, AMX and mono chamber cells*

The evolution voltages of the three MFCs (Nafion, AMX and mono-compartment) were investigated respectively and results are shown in Fig. 2. During the course of the experiment, the voltages of the Nafion and AMX MFCs increased a little bit during the first 25 hrs and remained almost constant (0.015 V). The initial phase before the rapid rise in voltage, is characteristic of a phenomenon related to the growth of microorganisms. This behavior corresponds generally to a pattern of growth due to the necessary adaptation of the microorganisms to the growing conditions before starting the exponential growth. Then, 2 mL of glucose (0.1 mol/l) were added in the anolyte, to stimulate the bacterial growth. As a result the voltage increased as result sharply up to 0.100 V for Nafion cell where it remained constant during 100 hrs of functioning. However, with AMX cell the voltage did not change. But, when the discharge resistance was changed from 1k Ω to 20 k Ω, both voltages rose sharply to reach the peak of 0.174 V for Nafion cell and 0.137 V for AMX cell until 123 hrs. Moreover, in order to increase the reduction proton at the cathode, 2 mL of HCl (0.001 mol/l) were added in the catholyte, the voltage rose steadily to reach the peaks 0.395 V and 0.487 V for Nafion and AMX respectively. After, they dropped off and leveled out at 0.035 V and 0.150 V for Nafion and AMX respectively.

Besides, the voltage of the mono-compartment cell was high right up from the beginning until the end of the experiment. This result is in good agreement with previous studies carried out with garden soil leachate [22].

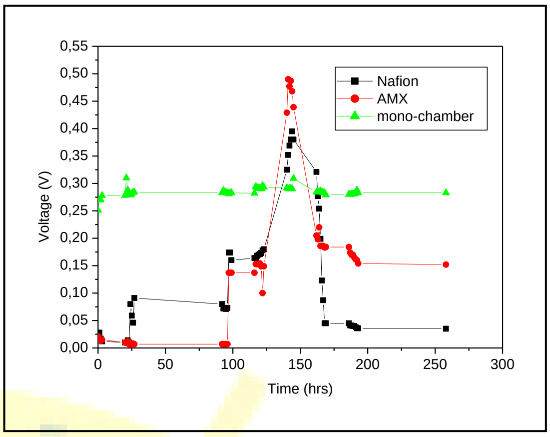


Fig.2: Voltages evolution of MFCs

B. *Electrochemical characteristics of MFC*

After closing the anode compartment (anaerobic condition), the power density was stable in both MFCs. The characteristic curves of polarization and power were used to evaluate the electrical performance of the cell. The polarization was obtained using different values of the resistance ranging between 10 Ω and 10 MΩ.

As shown in Fig.3, the polarization curve presents three distinct regions. In effect, owing to the activation resulting from the energy loss during the initiation of the Ox/Red reactions and electron transfer between the bacterial cell and the anodic surface, the MFC started by creating a short-circuit current density at the highest voltage. Then, it exhibited an ohmic linear drop caused by the electrolyte. And at last, it yielded the maximum open-circuit current density due to the loss of concentration occurring during the diffusion phenomenon.

On the other hand, the power curve represented in Fig.4, provides the maximum energy that can be delivered by the MFC. As predicted by the literature, the power density increased with increasing values of current density, and reached optimal values. In effect, the maximum specific powers produced by the AMX and Nafion MFCs were respectively 1.10 mW/m2 and 0.45 mW/m2, but the current at the maximum power was less important for MFC/Nafion (2.5 against 5 mA/m2 for MFC/AMX. In contrast, after 11 days of operation, the power produced by the mono-compartment fuel cell gave the highest so far obtained (11.90 mW/m2). Besides, the current drops observed with the AMX and Nafion MFCs, near the short-circuit conditions showed limits in terms of flow of reagents or reaction products, leading to unstable states of the systems.

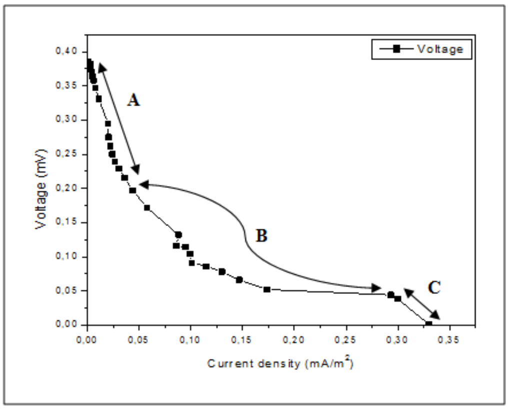
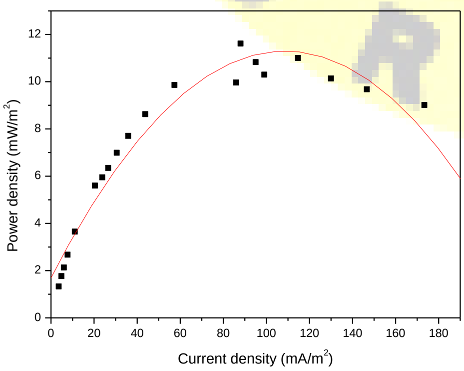
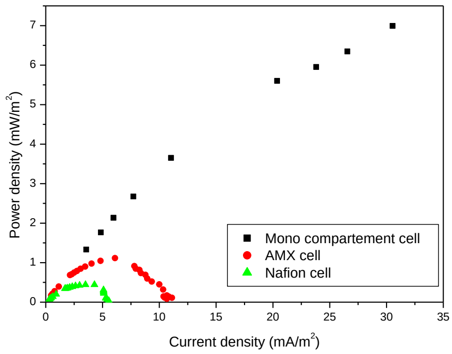


Fig. 3 Typical polarization curve of mono-compartment MFC



(a)



(b)

Fig. 4: Power density curves of MFCs: (a) mono-compartment and (b) cells grouped together

IV. CONCLUSIONS

The nafion membrane is recognized to be the best separator so far used in hydrogen fuel cells, because of its higher proton conduction. However, its use in the microbial fuel cell seems to be less efficient, because the metal ions present in the anolyte enter in competition with the proton, making the catholyte more basic, thus less reduction of protons at cathode. In contrast, the anion exchange membrane AMX was successfully applied where the metal ions present in the wastewater anolyte compartment, were blocked by the membrane giving way to the protons to displace freely and be reduced efficiently at the cathode. Whilst in the mono-compartment cell, the ions moved sideways between anode and cathode, yielding the highest power density so far obtained.

Besides their advantageous ecological role in converting polluted biomass into electricity, our elaborated MFCs are still facing practical barriers such as low power and current density. It seems qualitatively in good agreement with a research carried out recently (2015) by Rahimnejad et al., [23].

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