Influence of Membrane Type on Some Electrical Properties of a Single Microbial Fuel Cell

Hafsa Bouzidi
LMPMP and LEES Laboratories
Faculty of Technology
Ferhat Abbas University
Setif, Algeria
hafsabouzidi@yahoo.fr

Lhadi Otmani
URMES Laboratory
Campus El Maabouda
Ferhat Abbas University
Setif, Algeria
elhadi_otmani@yahoo.fr

Rachida Doufnoune
URMES Laboratory
Campus El Maabouda
Ferhat Abbas University
Setif, Algeria
doufnoune@yahoo.fr

Larbi Zerroual
LMPMP Laboratory
Faculty of Technology
Ferhat Abbas University
Setif, Algeria
zerroual@yahoo.fr

Djafer Benachour
LMPMP Laboratory
Faculty of Technology
Ferhat Abbas University
Setif, Algeria
bendjafer@univ-setif.dz

Received: 8 February 2022 | Revised: 27 February 2022 | Accepted: 14 March 2022

Abstract-The effects of different parameters on the electric output of air-cathode microbial fuel cells were investigated in this work. The single microbial fuel cell was equipped by modifying Proton Exchange Membranes (PEM). Two membrane types were prepared: first by using the combination of Poly Vinyl Alcohol (PVA) with Polystyrene Sulfonate (PSSNa), while the second membrane was elaborated by mixing Poly Vinyl Chloride (PVC) with Methyl Tri-Octyl Ammonium (MTOA) chloride. The PEMs were incorporated into the air-cathode to form a Membrane Electrode Assembly (MEA) to promote electricity generation. PVA/PSSNa and PVC-MTOA membranes were synthesized by solution casting method. Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet (UV) Visible spectroscopy, Scanning Electronique Microscope (SEM), Differential Scanning Calorimetry (DSC), and water Contact Angle (CA) were used as characterization techniques to explore the membrane structure and properties. The performance and the electric capacity of the microbial fuel cell in real time were operated using an external resistance of 5kΩ. Impedance and resistance capacity were determined using the polarization method. It was found that the internal resistance of the PVA/PSSNa and PVC-MTOA membranes were 50 and 350Ω respectively. The voltage values at open circuit of the cells using PVA/PSSNa and PVC-MTOA membranes were 600mV and 150mV respectively. The values of power, current, and power density, are quite interesting. Cells with PVA/PSSNa and PVC-MTOA membranes gave values of 18.24 and 9.64mW.cm² respectively.

Keywords-PVA/PSSNa; PVC-MTOA; membrane; single microbial fuel cells; renewable energy; wastewater

I. INTRODUCTION

Human sustainability is determined by deriving factors, among which energy is the most important. During the last decade, fossil fuel commodity has seen a sharp decline because of the harmful effects of fossil fuels on the environment [1]. The problem of pollution pushes the researchers to look for new sources of energy, such as renewable energy [2]. Promising results were acquired by different renewable energy sources, such as solar, wind, tidal, geothermal, and biomass. In the last few years, the research into alternative sources of renewable energy has increased exponentially [3]. However, a new source of energy which is sustainable and environmentally stable was needed [4]. Wastewater treatment is a new energy technology and a bio-energy source [5-6]. The bio-energy process [7] involves the use of microbes to produce electricity. This technology is considered to have tremendous potential [8]. The bacteria available in a bio-convertible substrate were directly used as a catalyst to convert chemical energy to electricity in [9]. It is known that bacteria can generate electricity from organic waste sources [10]. A renewable process was used to generate energy in the form of electricity, in consistent fresh, resourceful manners, through the use of the Microbial Fuel Cells (MFCs) [11]. It was found that in MFCs, energy can be recovered from wastewater treatment, in fact from a wide range of organic compounds present in wastewater [12].

The MFCs consist of two compartments: anodic and cathodic. MFCs are composed of one anodic chamber filled with wastewater and an air cathodic chamber. The anode compartment includes domestic or industrial wastewater with sludge, and the cathode compartment is either used to remove heavy metals or for denitrification [9]. Many MFCs play an important role in producing bio-energy, such as value-added chemicals, via an easy operation, and at low maintenance cost [13]. The removal of organic constituents of wastewater leads
to the electricity production from the chemical energy stored in chemical bonds [12]. Three mechanisms to generate bioelectricity have been proposed: direct electron transport via membrane bound proteins (e.g. cytochromes), conductive nano-wires, and indirect shuttles via redox mediators (e.g. riboflavin) [14]. With regard to the source abundance, high efficiency, and convenient transportation, the most promising energy conversion devices are Proton Exchange Membranes (PEMs) [15]. PEMs are the most important factor to transport protons, and Nafton membrane has been widely used due to its high conductivity.

Recently, numerous studies have been conducted to find alternative membranes [16]. Desirable PEMs require excellent characteristics, the most important of which is high and stable proton conductivity [17]. An electron flow through the electrodes producing bioelectricity, has been demonstrated experimentally by the bacterial degradation in wastewater [18]. Microbial electricity production offers the possibility of obtaining electrical current from a wide range of soluble or dissolved organic wastes such as artificial, real, and biomass lignocellulosic wastewater [19]. The most important advantages of MFC are wastewater treatment, application of micro-organisms, energy production, and inexpensive biocatalysts [12]. Since the production of electricity in MFCs is related to wastewater treatment, it is considered as one of the most attractive energy sources [20]. MFCs are an emerging technology for simultaneous treatment of wastewater and energy recovery [21], following a similar concept to traditional fuel cells [3]. The process of MFCs was based on the generation of bioelectricity, and this method has been leaded by the bio-potential developed between the bacterial metabolic activity and the electron acceptor conditions, separated by a membrane [22].

The use of MFCs is one potential alternative energy source [3]. The reduction of electron acceptors, with electricity, was harvested in a circuit, by the anode which collected organics oxidized by the electrogenic microorganisms and combined with protons to cathode. The electricity generation and stability of MFCs are radically affected by the microbial communities on the electrode surface [23]. MFC operation includes several steps: first, the carbon dioxide is digested from bacteria and the produced electrons are not directly transferred from bacteria to their electrons acceptor. The transport process is realized over other factors: cathode, anode, resistance, and membrane which transfer protons to the cathode [26-27]. When the MFCs are operated independently of an electrical device and as an integrated part of an electrical grid that controls the fuel cell output, an external resistance is used to dissipate the electrical energy [20]. The separator is an important factor that affects the design of MFCs [28], which is used to separate anode and cathode. The Cation Exchange Membrane (CEM) and PEM, are investigated as the most important effect in the system: a membrane permits the proton passage and not the substrate, using an organic medium [29-34]. Recently, authors in [9] proposed that the factors which can lower the internal resistance in the MFC, should be optimized to obtain the highest values of voltage density and power.

Most works cited in the literature deal with the use of fuel cells in electrochemical application (batteries), at an industrial scale. In the present work, a new strategy in MFC (single chamber) has been tested using two different PEMs. Combined with a resistance, this separator was based on the order: PVA with PSSNa, and PVC, while the MTOA membrane was used as a cathode material.

II. MATERIALS AND METHODS

PVA with a molecular weight of 130,000 (99% hydrolyzed powder), PSSNa powder with a molecular weight of 70,000, glutaraldehyde (GLA), PVC powder with a molecular weight of 93.92g/mol, MTOA as ionic liquid with a molecular weight of 404.16g/mol, and tetrahydrofuran (THF) with a molecular weight of 72.10g/mol, which was used as a dissolving agent, were all provided by Sigma-Aldrich and were used as such without any further purification. Figure 1 shows the diagram of the experimental procedure.

A. Membrane Preparation

1) PVA-PSSNa Film Preparation

As a first step, 1.5g PVA were dissolved in deionized water and the obtained solution was stirred at 80°C until the PVA particles were completely dissolved. At the same time, the PSSNa solution was prepared by dissolving 0.6g in deionized water. The obtained mixture was further stirred at room temperature until the stabilization of the solution. As a second step, GLA was poured dropwise to the solution and then few drops of HCl solution were added. It is worth noting that a simple pouring of the mixture into a glass sheet with a uniform surface and similar thickness was realized. Finally, the thin film was dried at room temperature for a day.

---

**Fig. 1.** Experimental diagram.
voltage values were recorded with an Arduino program. The VOC was measured with a digital multi-meter. The real time stainless steel, left to dry in open air. The Voltage Open Circuit (VOC) was measured using a thermogravimetric analysis (TGA PERKIN-ELMER) apparatus in which the temperature range was set from 25 to 500°C, with a heating rate of 10°C/min. The surface morphology of the membranes was observed by SEM (JEOL, JSM 6510 LV) and the analysis was operated at an acceleration voltage (5kV). The signal scans of 32 were realized in the temperature range of 35-350°C, where the cross-section area (cm²) and R the resistance (Ω).

A Nyquist plot was used to determine the internal resistance of the system after applying the electrochemical impedance spectroscopy technique. Equation (2) gives the relation between the impedance system and the ionic conductivity:

\[
\sigma = \frac{L}{\pi A R_A} \tag{2}
\]

where σ is the ionic conductivity (S/cm⁻¹), L the thickness (cm), A the cross-section area (cm²) and R the resistance (Ω).

### III. RESULTS AND DISCUSSION

#### A. Spectroscopic Characterization and Morphological Studies

1) FTIR Characterization

PVA-PSSNa was obtained from the reaction of PVA-PSSNa and GLA. The FTIR spectra confirmed the chemical structure. Figure 2 shows the FTIR spectra of PVA-PSSNa. The very wide band that appears at 3356cm⁻¹ is related to the stretching vibration of hydroxyl groups of PVA chains. The 2931cm⁻¹ band is attributed to alkanes, and ester and ether bands are registered at 1715cm⁻¹ and 1435cm⁻¹. The symmetric and asymmetric stretching vibrations due to the sulfonic group are located at 1125cm⁻¹ and 1240cm⁻¹ respectively. The broad band at 1125cm⁻¹ indicates the linking of sulfonic anion with phenyl ring. Additionally, the aromatic functional groups of PSSNa

where \( \eta \) is the swelling rate (%), and \( m_f \) and \( m_i \) are the final and initial weight of the membrane (g) respectively.

\[
\eta = \frac{m_f - m_i}{m_i} \times 100 \tag{1}
\]
chain are located at 840 cm\(^{-1}\). In the FTIR spectra of PVC-MTOA membrane, the band located at 3673 cm\(^{-1}\) is associated to a strong free alcohol related to a bond interaction between PVC and MTOA in the presence of the THF as solvent agent. The located bands at 3000-3100 cm\(^{-1}\) present an amine deformation of the MTOA. A strong alkane C-H band is situated at 2109 cm\(^{-1}\), the band recorded at 965 cm\(^{-1}\) confirmed the existence of the alkene. The appearance of a broad absorption band at 1628 cm\(^{-1}\) was related to the linked N-H, the bands at 1460 cm\(^{-1}\) and 1248 cm\(^{-1}\) indicated the C-H and C-C bonds respectively, an alcohol group was located at 1378 cm\(^{-1}\), and chloroalkane C-Cl was located at 723 cm\(^{-1}\).\(^{[35-36]}\)

Fig. 2. FTIR spectra of (a) PSSNa/PVA membrane and (b) PVC/MTOA.

2) DSC Characterization

The DSC thermograms are illustrated on Figure 3.

Fig. 3. DSC curve of (a) the blend PVA/PSSNa, (b) the blend PVC/MTOA.

As mentioned above, the mixture was stable and has good miscibility between polymers, thus no visible phase separation between PVA and PSSNa was detected. This confirms the morphology results obtained by SEM. In addition, the thermograms revealed a single glass transition temperature (\(T_g\)) of the blend in the range of 60 to 90°C, which indicates the total miscibility of the polymers. In the DSC curve obtained on PVC/MTOA membrane, a sudden change in heat transfer at 165.5°C is noticed. This may be explained by the irregularly shaped samples, the ionic liquid being more flexible than the PVC, results in a flexible membrane compared to the PVA/PSSNa membrane. The second endothermic peak at 221°C related to the crystallization temperature (\(T_c\)) corresponds to the side reaction and decomposition of the membrane while the third peak at 245°C corresponds to the melting point temperature. At high temperature all the interactions between the chains are broken.

3) SEM Characterization

SEM images of the membranes are presented in Figure 4. A micrography of the mixture formed by blending PVA, PSSNa, GLA, is also reported in the same Figure.

As can be seen in Figure 4, no phase separation was observed for the prepared membranes. The PVA/PSSNa presents a good combination between the two polymers and homogenous surface. PVC/MTOA membrane exhibits a smooth and homogeneous nonporous surface too. The obtained membranes are transparent and have good clarity, implying good compatibility between the ionic liquid and the polymer. This leads to more contact area and more compatibility to form a bio-film (in which the ionic charge is produced because it is formed with the bacteria found in the medium).

4) Contact Angle and Swelling Rate Characterization

The hydrophilicity of the membranes was evaluated using the water CA technique. It can be noted that for PVA/PSSNa membrane the values varied from 35.6° to 36.9°, while for PVC/MTOA membrane, the contact angle values varied from 12.3° to 12.7°. The polymers containing sulfonic acid groups
transport protons via the vehicular mechanism, relying on the presence of water PVA/PSSNa membrane. The water adsorption of the PVC/MTOA membrane is attributed to the ionic liquid group. Table I summarizes the CA and the swelling rate values of PVA/PSSNa and PVC/MTOA membranes, it confirms the results observed in Figure 4.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle (°)</th>
<th>Swelling rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA/PSSNa</td>
<td>35.6-36.9</td>
<td>78.38</td>
</tr>
<tr>
<td>PVC/MTOA</td>
<td>12.3-12.7</td>
<td>86.07</td>
</tr>
</tbody>
</table>

The water absorption of the two membranes was studied by immersing the membranes in deionized solution. The weight of the membranes was measured before and after immersion. The membranes show that the water uptake was elevated due to water molecule mobility. The elevated water-uptake improves the swelling rate of PVA/PSSNa ($\eta = 78\%$) and PVC/MTOA ($\eta = 86\%$) membranes. The problem encountered is that the membranes never return to their initial states after being immersed in water. Consequently, the membranes have a good water uptake, and this will increase the proton conductivity.

5) TGA Characterization

The thermal stability of PVA/PSSNa and PVC/MTOA membranes under nitrogen atmosphere, was evaluated by thermogravimetric analysis. The TGA thermograms are presented in Figure 5.

![Fig. 5. TGA curves of (a) the blend PVA/PSSNa, (b) the blend PVC/MTOA.](image)

The thermogram shows a typical three-step degradation of PVA/PSSNa. A small weight loss was observed at about 61°C due to the evaporation of physisorbed water. The second weight loss, which occurred between 217 and 462°C, corresponds to the degradation of PVA/PSSNa. The third weight loss, above 465°C, was due to the decomposition of the backbones of the materials. The curves showed a typical two-step degradation pattern of the PVC/MTOA membrane. No obvious weight loss was observed until 250°C. The weight loss recorded between 253 and 415°C corresponds to the degradation of PVC, whereas the second weight loss in the range 415-495°C is due to the decomposition of MTOA.

6) UV Characterization

The UV spectra of PVA/PSSNa and PVC/MTOA are presented in Figure 6. The main peaks are located at 227-193.5nm and are attributed to PVA/PSSNa and PVC/MTOA respectively, which indicates a significant interaction between polymers, while no phase separation was noticed.

![Fig. 6. UV visible spectra of (a) PSSNa:PVA and (b) PVC/MTOA membranes.](image)

After the discharge of the cells, it was noticed that the internal resistance was approximately 62Ω for the PVA/PSSNa membrane. Almost no difference in the internal resistance value before and after the test was detected, while in the case of PVC/MTOA membrane, the internal resistance significantly increased at the end of the test (1200Ω). This difference can be related to the membrane aging. The ionic conductivities of the PVA/PSSNa and PVC/MTOA membranes are respectively $1.02\times10^{-4}$ and $8.37\times10^{-6}$S/cm. PVA/PSSNa presents higher proton conductivity compared to PVC/MTOA (see Table II).
High electron transfer from the anodic chamber to the cathode leads to high current. The anode potential should be low and the cathode potential should be high in order to have a maximum fuel cell performance. The metabolic activities of the biocatalyst and the respective energy dissipation can affect the anode potential. In a biofuel cell, bacteria drain off their electrons to the anode.

Figure 8 shows the polarization curve of MFCs filled with wastewater. The two curves describe the voltage and power as functions of the current density to identify the maximum output power density of MFCs. The obtained open circuit voltage was 604mV for the PVA/PSSNa and 156mV for PVC/MTOA (Table III). Figure 9 shows the polarization curve of MFCs filled with medium. The power and the current density increased after four weeks in the case of the PVC/MTOA membrane but the voltage decreased from the first week. The maximal values were obtained in the second week of using the medium and were 9.64mw/cm² power and 0.10mA/cm² current density.

Regarding the PVA/PSSNa membrane, the maximal values were observed during the first week and they were about 18.24mw/cm² power and 0.14mA/cm² current density. The cell decreased after that and this decrease of power generation can be related to the structure and to the effect of the internal resistance of the two membranes: the PVC/MTOA membrane is more flexible (from the mechanical point of view) and more
resistant (from the electrical point of view) than the PVA/PSSNa membrane. This difference will impact the biofilm formed, while the PVA/PSSNa will be more effective in the electricity generation. Accordingly, the electron transfer from the anodic chamber to the cathode decreases according to the biofilm forming the electrical resistances of the electrodes, the membrane internal resistance and electrolyte, the power drops due to the increasing Ohmic losses, and the electrode overpotential with the point where no more power is produced [37-39].

In a previous similar work [21], the authors used a PVC-based membrane, however the conductivity obtained was not as good as the one obtained in this study for the PVC/MTOA membrane. In addition, we used the CA parameter to evaluate the membrane surface capacity for matter adsorption, which, to the best of our knowledge, is reported for the first time.

IV. CONCLUSION

In this paper, MFCs were used to directly generate electricity from the oxidation of dissolved organic matter. However, the optimization of MFCs requires more knowledge about the factors that can increase the power output such as the capacity of proton exchange system which can affect the system characteristics, particularly the internal resistance and the external resistance. The power (P) was calculated according to $P = IV = (I/V)R$, where $I$ is the current, $V$ is the voltage, and $R$ is the resistance. The prepared assisted cross-linked PVA-PSSNa membrane has a good ionic conductivity and a good miscibility and thermal stability. In addition, it exhibits high proton exchange capacity and lower internal resistance, compared to the PVC/MTOA membrane which has a high internal resistance and a long term to discharge. It has also good miscibility, a hydrophilic character, and a good thermal stability.

AUTHORSHIP CONTRIBUTION STATEMENT

The results presented here are part of a Ph.D. thesis work. H. Bouzidi, as a Ph.D. student, conducted most of the experimental and characterization work. L. Otmani and R. Doufnoune prepared and provided the PVA-PSSNa membrane, L. Zerroual (thesis co-advisor) helped in the electrochemical experimental work, while D. Benachour (thesis advisor) did the editing.

REFERENCES


