

Reinforced Proton Exchange Membranes for Single Chamber Microbial Fuel Cells

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ABSTRACT

The performance of microbial fuel cells (MFCs) is mainly determined by the catalytic activity at the electrodes, which depends on the catalyst's nature such as mechanical, conductivity. Nafion[®] has become the standard membrane basically used in this type of fuel cells and its use is limited due to the significant oxygen permeability from the air through the membrane of the microbial chamber cell. Sulfonated (poly-ether-ether-ketone), (SPEEK) is a good proton conductor. In this sense, blends of SPEEK with PVA (polyvinyl alcohol), a hydrophilic polymer, were prepared and it was observed that above 25 wt% PVA content the membranes were stable in boiling water, with acceptable proton conductivity. On the other hand, blends of SPEEK with a hydrophobic polymer, such as PVB (polyvinyl butyral), were prepared and above 30 wt% PVB content the membranes were also have mechanical, barrier methanol and oxygen properties were excellent while proton conductivity was very low. Thus, nanofibers of SPEEK-PVB were obtained and interestingly it was found an improvement of the intrinsic proton conductivity of the material. Finally, composite membranes containing nanofibers of SPEEK-PVB into a SPEEK-PVA matrix were prepared and characterized towards its use in MFCs. In this work we have focused on the synthesis and characterization of the reinforced proton exchange membranes: Nafion-PVA15, Nafion-PVA23, SPEEK-35 PVA SPEEK-35 PVB and SPEEK/PVA-PVB membranes with two different sulfonation degrees of SPEEK (1.75 and 2.05 meq/g ion-exchange capacity) for their utilization in microbial fuel cell applications (MFCs). Those membranes were characterized in single chamber microbial fuel cells (SCMFCs) using electrochemically enriched sodic saline inocula as biocatalyst. The results show that Nafion-PVA-15 conducted to a maximum power density of 1053 mW/m³ at a voltage of 0.340 V, which was superior to the behavior obtained on commercial Nafion-117, Nafion-PVA23, SPEEK-35PVA, SPEEK-35PVB and SPEEK/PVA-PVB base water. Electrochemical impedance spectroscopy characterization revealed a low total internal resistance (R_{int}) on Nafion-PVA-15 of 522 Ω when compared to other membranes. This could contribute to attain higher maximum powers in MFCs. Further characterization results studies would be directed towards the development of cost-effective procedures of membrane preparation for MFC.

1. Introduction

Microbial fuel cell (MFC) has emerged as a promising technology for waste water treatment as well as energy recovery by microorganisms, and has been an intensive subject in the bio-electrochemistry [1, 2]. Electrochemically active bacteria in the anode chamber are oxidizing the diverse organic substrate, separating electron and protons. These electrons and protons travel to the cathode, the former via an external circuit and the latter diffusing through electrolyte and a proton exchange membrane (PEM). The protons and electrons subsequently combine at the cathode with oxygen, to form water with aided by a catalyst such as platinum [3, 4]. The performance of MFC mainly are determined for each electron that is produced, an equivalent proton must be transported to the cathode through the electrolyte to sustain the current [5]. Therefore, PEMs are one of the most important components in MFCs, as they physically separate the anode and cathode chamber while allowing protons to pass through to the cathode. In MFCs, the Nafion 117 membrane is one of the most commonly used PEMs, though a number of problems associate with Nafion 117 are oxygen leakage from cathode to anode, substrate loss, cation transport and accumulation rather than protons, and biofouling. One of the main problems of these, oxygen leakage into the anode chamber can either inhibit the growth of obligate anaerobes or aerobic respiration by facultative bacteria, as a result of lower energy recovery due to the substrate losses [6-9]. Nafion contains negatively charged sulfonated groups in the backbone of membrane explains the high level of proton conductive property, while also showing a significant undesirable affinity for other cation rather than protons [10]. In general MFCs are operated at a neutral pH in order to optimize, biocatalyst in the anode chamber, while other cations (Na, K, Ca, Mg and NH_4) contained in growth medium are typically present at a 105 times higher concentration than protons. Subsequently, these cations combine with the sulfonated groups of Nafion and inhibit the migration of protons produced during substrate degradation, causing a decrease in MFCs performance due to the pH reduction in the anode chamber, with a corresponding pH increase in the cathode chamber [11]. In addition, the economic viability of MFCs is high while using Nafion.

Towards, the above problems have not been systemically examined in MFCs for their effect on power generation. Several attempts to increase membrane performance ranged from modification/reinforced conventional membrane to novel membrane such as earthen pot [12] and cellulose acetate micro-filtration [13]. Membrane included polytetrafluoroethylene (PTFE) or poly(-dimethylsiloxane) (PDMS) are tested on the air cathode in the MFCs [14, 15]. However, it was difficult to use thick earthen pot materials in MFC stacks [12] and the PTFE or PDMS applied on the air cathode increased the complexity of producing cathodes with consistent effective performance [14, 15]. Separator-less MFCs were based on the designs of existing conventional wastewater treatment process such as the two-stage process for nitrogen and phosphorus wastewater treatment [16] and the continuous anaerobic reactor [17]. The performance of separator-less MFCs was also improved by modifying their electrodes [18]. While novel nano-reinforced fiber membranes have reduced the cost of materials used in MFCs especially that of the PEM, there is no reported work yet on using separators made from sulfonated poly(ether ether ketone) (SPEEK) composite reinforced nano-fibers membranes and Nafion reinforced PVA nano-fiber membrane that are low cost than other PEM. SPEEK,

since it is a good proton conductor and its glass transition temperature lies around 200 °C. Therefore, the focus of this study is to synthesis of SPEEK with PVA (polyvinyl alcohol), SPEEK with PVB (polyvinyl butyral), Nafion-PVA15, Nafion-PVA23, SPEEK-35 PVA SPEEK-35 PVB and SPEEK/PVA-PVB membranes with two different sulfonation degrees of SPEEK (1.75 and 2.05 meq/g ion-exchange capacity) for their utilization in microbial fuel cell applications (MFCs).

2. Experimental Section

2.1. Preparation of membranes

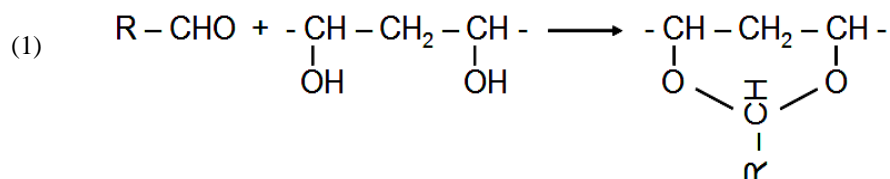
2.1.2. Nafion-PVA membranes

2.1.2.1. PVA nanofibers

Porous PVA mats were produced by a standard electrospinning setup (Yflow S.L.), Málaga, Spain) through the feeding of a water based solution of PVA (0.04:1:10 wt. CTAB:PVA:water). CTAB was used as surfactant in order to reduce surface tension of water and improve electrospinning ability. The distance between the needle and the planar collector was fixed at 22 cm, the solution flow rate at 0.5 ml/h, the voltage of the needle at +12 kV and the voltage of the collector at -5 kV. Mats electrospun during 8 hours showed a thickness around $120 \pm 10 \mu\text{m}$, meanwhile those obtained after 4 hours were aprox. $60 \pm 5 \mu\text{m}$. The collected mats were heated during 3 hours at 170°C in a vacuum atmosphere (250 mbar pressure) with the purpose of removing water and increasing manipulability.

2.1.2.2. Chemical functionalization of PVA nanofibers.

The PVA mats were fixed between round steel frames and then immersed into a bath with a 0.04 M concentration of the 4-formyl-1,3-benzenedisulfonic acid disodium salt and 0.1 M of chlorhydric acid as a catalyst for the schematic reaction (1), solved in a mixture composed of isopropanol/water (70/30 v/v):



Reaction was carried out at 60°C for 2 hours. The sodium ions present on the surface functionalized PVA nanofibers were exchanged with protons through immersion into a bath of isopropanol/water (70/30 v/v) containing chlorhydric acid with a 0.3 M concentration.

Ion-exchange was finished by washing of the mat with a solution of isopropanol/water (70/30 v/v) and further immersion in pure isopropanol. Finally, the mats were placed into an oven at 60°C for drying.

The last step was the crosslinking of the PVA chains in order to raise mechanical and thermal properties of the nanofibers. This was accomplished by reaction with glutaraldehyde vapor in a closed vessel during 24 hours at room temperature. At the bottom of such vessel a 50 wt% water solution of glutaraldehyde was placed and let it to evaporate slowly.

After the crosslinking process, the mats were heated at 100°C for 15 minutes with the aim to remove adsorbed glutaraldehyde and water. The crosslinked mats strongly increased their chemical resistance and they were not able to dissolve in boiling water.

2.1.2.2. Composite Nafion[®] membranes reinforced with PVA nanofibers

Once the mats of nanofibers were crosslinked, the following step was the preparation of the reinforced membranes using the previously crosslinking mats of PVA. For this, the functionalized and crosslinked mats, still mounted on the frame, were impregnated with the 5 wt% Nafion[®] solution in isopropanol and water (4/1 w/w, respectively).

Each impregnation step was carried out by wetting the PVA mat into the Nafion[®] dispersion for 5 min and followed by evaporation in an oven at 100°C for 5 min more. This was repeated 8 times in every mat so that an outer visible Nafion[®] layer was formed.

Such composite membranes obtained by infiltration of Nafion[®] into the PVA nanofibers were annealed at 125°C for 90 min under pressure in order to remove any residual solvent and enhance Nafion[®] can accommodate into the fibrillous structure.

Finally, the membranes were conditioned by treatment with water at 85°C for 30 min, followed by an oxidation with 3 wt% hydrogen peroxide during 1 hour at 80°C and further protonation by 1-hour ion-exchange with a 1 M chlorhydric acid solution at 80°C. Then, the composite membranes were washed with hot water at 85°C, dried and stored.

The thickness of the composite membranes (L) was dependent on the deposition time of the electrospun nanofibers mats, and it was measured with a digital length gauge (Heidenhain, model MT 12). The membrane thickness was calculated from the average value after ten measurements on different parts of the sample. The pertinent results are given in Table 1.

2.2. SPEEK-based membranes

2.2.1. Water-based SPEEK-35PVA membranes

SPEEK with ion-exchange capacity (IEC) of 1.75 meq/g was dissolved in boiling water. An appropriate amount of PVA was separately dissolved in water at 80°C (10 wt% PVA concentration) and then both solutions were mixed to prepare a SPEEK-35%PVA composition (wt. proportion) and water was added until reaching a 7.5 wt% total polymer concentration. The solution was stirred at room temperature until complete homogenization and the membranes cast on a Teflon® Petri dish overnight in an oven at 40°C. Finally, the membranes were crosslinked at 120°C for 1 hour and placed in boiling water for another hour. The membranes were stored in water at room temperature.

2.3. DMAc-based SPEEK-35PVA membranes

Membranes were prepared by casting of solutions with a 10 wt% concentration of polymer blend (SPEEK+PVA) in DMAc solvent incorporating LiCl. Previously, LiCl was dissolved in DMAc at a 0.4 wt% concentration at room temperature. Then, the required amount of PVA was dissolved stirring at 140°C for 1 hour and afterwards the solution was let to cool down to room temperature. Finally, SPEEK (IEC=1.75 meq/g) was added and the solution stirred at 140°C for 1 hour in order to ensure a complete homogenization. Membranes were obtained by casting at 80°C on a Teflon® dish overnight, followed by a treatment at 140°C for 2 hours and 1 hour further at the same temperature under vacuum atmosphere with the purpose of enhancing the removal of trapped DMAc molecules. The last step was crosslinking between the SPEEK and the PVA chains at 200°C for 1 hour (without vacuum). It was observed that crosslinking did not take place below 170°C in opposition to the behavior of the water-based SPEEK-35PVA membranes. Finally, the crosslinked membranes were immersed in boiling water for 1 hour and stored in water at room temperature.

2.4. SPEEK-PVA-PVB membranes

2.4.1. SPEEK-30PVB nanofibers

First, a SPEEK solution in DMAc with 30 wt% of PVB (SPEEK-30PVB) was prepared as follows: A required amount of PVB was dissolved under stirring in DMAc at 80°C for 1 hour. The solution was let to cool down at room temperature and then SPEEK (IEC = 2.05 meq/g) was incorporated and the mixture stirred for 1 hour at 80°C until complete homogenization (17.5 wt% total polymer concentration).

Nanofiber mats of SPEEK-30PVB were obtained by electrospinning (YFLOW SL, Malaga, Spain). A potential difference of 35 kV was applied between the needle and the planar collector, which were separated 25 cm, and a flow rate of 0.2 ml h⁻¹ was fixed during the electrospinning process. After 15 hours deposition, the mat was heated at 160°C for 30 minutes to remove trapped DMAc and then crosslinked at 200 °C for 1 hour. For the crosslinking, the corresponding round frames were placed on the surface of the nanofibers to compensate the slight shrinking of the mat and keep tense the contained mat within the frames. Consequently, additional frames were mounted on the reverse sides in order to fix tightly the crosslinked nanofiber mats.

2.4.2. Composite membrane of SPEEK-35PVA reinforced with SPEEK-30PVB nanofibers

A water-based solution of SPEEK-35PVA (7.5 wt% concentration) was used for infiltration within the nanofibers. In this method, the nanofibers were immersed in the cited solution for 5 minutes and then placed in a climate chamber at 90°C with very low humidity level for other 5 minutes. This process is repeated 4 times spinning 90° the nanofiber mats in each step. In the final step, the mat is left in the climate chamber during 10 minutes to enhance the drying of the formed composite membrane. Then, the membranes were cut along the borders of the frames and left at room temperature overnight to ensure total dryness.

Finally, 5x5 cm² membranes were cut and crosslinked at 120°C for 1 hour in a hot plate press under a pressure of 100 kg/cm². Similarly, the prepared composite membranes were boiled in water for 1 hour and stored in water at room temperature.

2.5. Characterizations of Nafion/PVA composite membranes

2.5.1. Water uptake

Water uptake was calculated from the difference between the weight of the membranes wet and dry, according the following expression,

$$\text{Water uptake (\%)} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \quad (1)$$

Since solubilization of some amounts of polymer from the as-prepared membranes was possible to occur during treatment in boiling water, the blend membranes were weighed after 1 hour in boiling water (m_{wet}) and after 3 hours in an oven at 100°C followed by other 3 hours in vacuum at that temperature (m_{dry}). This operation was repeated three times for giving an average value.

In table 1 we can see the values of the water uptake for the membranes used in this study.

2.5.2. Ion-exchange capacity (IEC)

To determine the ion-exchange capacity, the membranes in the proton form were treated with 50 ml of 2 M NaCl solution for 1 day. After this time, this solution was titrated with 0.01 M NaOH against a fenolftaleine indicator and the IEC calculated from the following equation

$$IEC \text{ (meg / g)} = \frac{V_{NaOH} \times 0.01}{m_{dry}}$$

The pertinent results of the IEC are given in table 1.

Table I. Thickness, water uptake, ionic exchange capacity and nanofiber deposition time for composite Nafion-PVA and SPEEK-PVA-PVB membranes, and for blend SPEEK-PVA membranes prepared in different solvents. Nafion[®] is included for comparison.

Membrane	Hydrated thickness (μm)	Water uptake (%)	IEC (meq/g)	Deposition time (h)
Nafion-PVA-15	15±1	21.2±0.1	0.46	3
Nafion-PVA-23	23±2	21.8±0.1	0.35	6
SPEEK-35PVA(Water)	122±7	152±7	0.47	-
SPEEK-35PVA (DMAc)	185±3	490±12	0.71	-
SPEEK-PVA-PVB	102±12	93±9	0.31	15
Nafion-117 (commercial)	216±4	21.5±0.1	0.91	-

2.6. Construction of single chamber microbial fuel cell

Construction of a single chamber microbial fuel cell (SCMFC) details can be found elsewhere [19]. In summary, the MFC consisted of a vertical cylinder built in glass, 9 cm long and 5.6 cm internal diameter (200 mL capacity). An assembly of anode-proton exchange membrane-cathode (AMC) was fitted at the bottom of the cell. The AMC, in turn, consisted of (from top to bottom) a perforated stainless steel plate 1 mm thick, a Toray flexible carbon cloth sheet (surface area of 0.0023 m², it performed as the anode) placed on the low circular face of the steel plate, a proton exchange membrane such as Nafion 117, Nafion-PVA15, Nafion-PVA23, SPEEK-35 PVA SPEEK-35 PVB

and SPEEK/PVA-PVB membranes, containing 0.5 mg cm^{-2} Pt catalyst loading (10 wt%/C-ETEK), a cathode made of Toray flexible carbon cloth, and a perforated plate of stainless steel 1 mm thick [19].

2.7. Linear sweep voltammetry and electrochemical impedance spectroscopy studies. Characterization of microbial fuel cells

The single chamber microbial fuel cell was characterized by linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) [19]. Linear sweep voltammetry (LSV) was performed in a Potentiostat/Galvanostat PARSTAT 2273, run at a recommended scan rate of 1 mV s^{-1} , starting from the measured open circuit potential to 50 mV [20, 21]. Impedance spectra of microbial fuel cells were obtained at the open circuit potential (E_{ocp}). The amplitude of the signal perturbation was 10 mV peak-to-peak, scanned in the frequency range of 100 kHz to 1 mHz. Data fitting was accomplished by Z-view software.

3. Results and discussion

We were characterizing the different Proton exchange membrane in single chamber microbial fuel cells (SCMFC) using electrochemically enriched sodic saline inocula as biocatalyst [2].

Nafion-PVA-15 showed a maximum power density of 1053 mW/m^3 at voltage of 0.340 V than the Nafion-117, Nafion-PVA-23, SPEEK-PVA-PVB, SPEEK-35-PVA Agua, and SPEEK-35-DmAC (Shown in Table. 2). Electrochemical impedance spectroscopy characterization reveals the less total internal resistance (R_{int}) of Nafion-PVA-15- 522Ω when compare to other membrane. This will pave to attain the maximum power in SCMFCs. When compare our results with previous literature in Table 3. We are got the highest power density without any additional input energy (agitation, circulation, and air purging)

Table 2. SCMFCs characterization with different Proton Exchange Membrane

Type of Membrane	Current Density (mA/m^3)	Power Density (mW/m^3)	Voltage(V)	Resistance $=R_{an}+R_{ca}+R_{mem+Sol}$
Nafion-117	3009 ± 03	913 ± 05	0.304	$620+227+0.53$
Nafion-PVA-15	3099 ± 04	1053 ± 02	0.340	$427+94+0.97$
Nafion-PVA-23	2465 ± 09	642 ± 07	0.260	$2158+41+0.83$
SPEEK-PVA-PVB	2817 ± 08	813 ± 01	0.288	$1136+2+3.4$
SPEEK-35-PVA	2438 ± 05	722 ± 18	0.296	$1460+1.9+3.5$
SPEEK-35-PVB	539 ± 15	245 ± 4	0.454	$2311+20.63+18.17$

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Table 3. Comparison of our Max power density with pervious literature value Membrane

Type of Membrane	Power Density (mW/m ³)	Cathode type	References)
Nafion-117	913	Air Cathode	Our work
Nafion-PVA-15	1053	Air Cathode	Our work
Nafion-PVA-23	642	Air Cathode	Our work
SPEEK-PVA-PVB	813	Air Cathode	Our work
SPEEK-35-PVA	722	Air Cathode	Our work
SPEEK-35-PVB	245	Air Cathode	Our work
Disulfonated poly (arylene ether sulfone)	616	Air Cathode	22
Nafion 212	488	Air Cathode	22
Anion Exchange Membrane	925	Air Cathode	23
poly(ether sulfone)-SPEEK-5%	235	Air Cathode	24

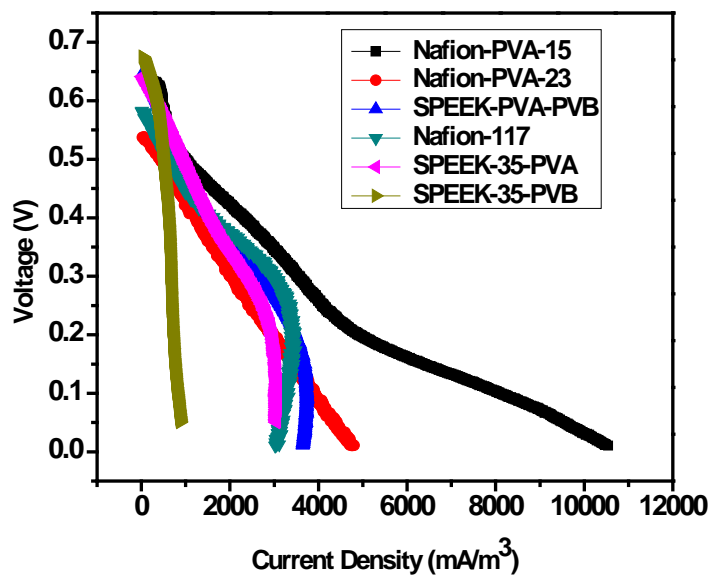


Figure. 1 Polarization Curve of the SCMFCs seeded with different proton exchange membrane

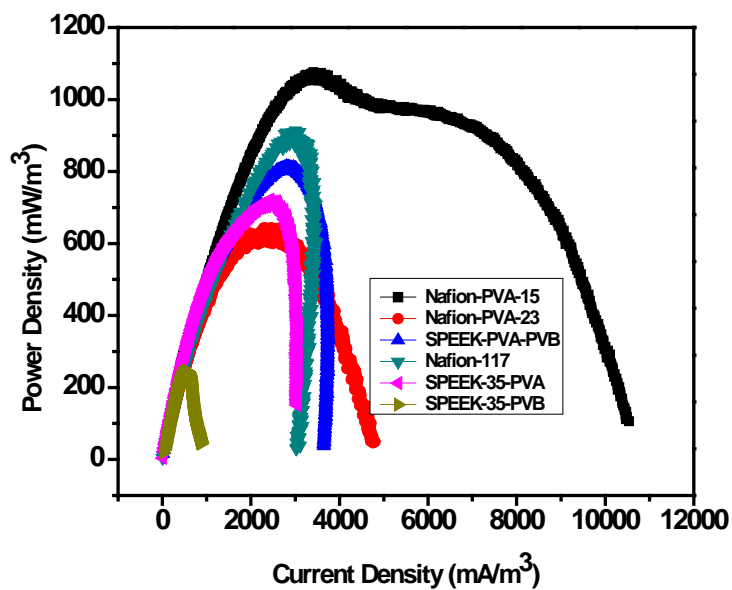


Figure. 2 Power density Curve of the SCMFCs seeded with different proton exchange membrane

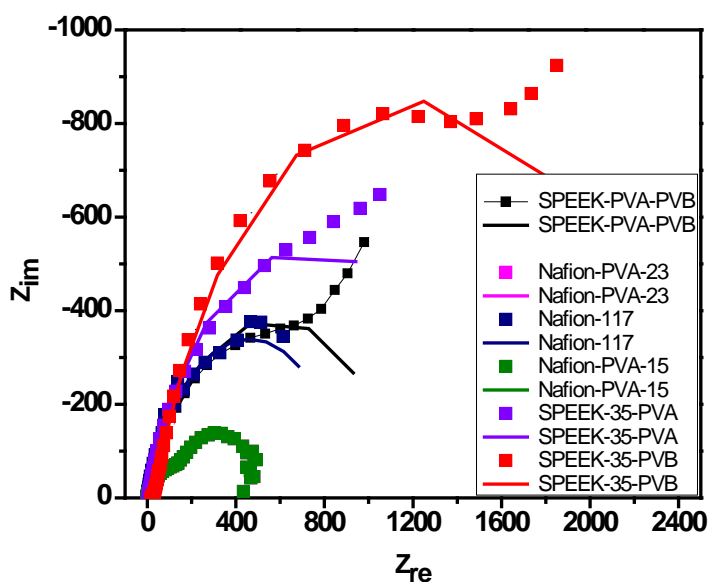


Figure. 3 EIS spectrum of the SCMFCs seeded with different proton exchange membrane

4. Conclusion

The results show that Nafion-PVA-15 conducted to a maximum power density of 1053 mW/m^3 at a voltage of 0.340 V, which was superior to the behaviour obtained on commercial Nafion-117, Nafion-PVA23, SPEEK-35PVA, SPEEK-35PVB and SPEEK/PVA-PVB base water. Electrochemical impedance spectroscopy characterization revealed less total internal resistance (R_{int}) on Nafion-PVA-15 of 522Ω when compare to other membranes. This will pave to attain the maximum power in MFCs. Characterization results were attracted towards the cost effective and amend preparation of microbial fuel cells.

5. Acknowledgements

The authors wish to thank SEP and CINVESTAV-IPN for granting a D.Sc fellowship to one of the authors (KSK). We gratefully acknowledge the financial support of the National Council of Science and Technology, CONACYT, under grants 101537 and FOINS 75/2012.

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