

# Synthesis and Properties of Sulfonated Poly (Maleimide) for Proton Exchange Membranes in Fuel Cells

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**ABSTRACT**— *In this paper, the synthesis and characterization of new sulfonated poly(maleimide) is described. Two-step polymerization method was used to prepare the sulfonated poly(maleimide) from maleic anhydride (MA) and p-dimethylamino-azobenzenesulfonic acid (DMBSA). The sulfonation degree of the polymer was regulated through variation of the molar ratio of DMBSA. Flexible, transparent, and mechanically strong membranes were successfully obtained. The membranes were characterized with Fourier transform infrared spectra, <sup>1</sup>H NMR, thermogravimetric analysis, ion-exchange capacity, and proton conductivity measurements. These results showed that the membranes had good thermal stability and exhibited high conductivity.*

**Keywords**— Microbial fuel cell, PEM membrane, Poly (maleimide).

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## 1. INTRODUCTION

The desire to develop alternative sources of energy to reduce the consumption of fossil fuels is globally shared. One of the many areas of research aimed at achieving this objective is the field of proton exchange membrane fuel cells (PEMFCs). These energy conversion devices have the potential to power automobiles, homes and other buildings, and portable electronic devices in a manner that is both environmentally friendly as well as potentially very efficient (60–70% or more) [1] and [2]. An essential component of every PEMFC is its proton exchange membrane (PEM). A successful PEM must possess several characteristics including high-protonic conductivity, impermeability to fuel and oxidant feed streams, good mechanical properties to ensure its durability, and cost effectiveness [3-5]. The current PEM standard is Nafion<sup>®</sup>, a poly(perfluorosulfonic acid) manufactured by the E.I. duPont Company, which provides good proton conductivity, chemical stability, and mechanical stability at temperatures up to 80°C with sufficient hydration [6]. In addition to its strengths, however, Nafion<sup>®</sup> also exhibits formidable limitations including cost, fuel permeability, and decreased performance accompanying loss of hydration above 80 °C. However, although Nafion, used the current PEM standard for commercial, possesses several desirable characteristics for PEMFCs use at low temperatures, including oxidative stability, good proton conductivity, and mechanical strength [7-14]. It's not enough. Thus, it displays lose of water, and low mechanical strength at higher temperatures [15]. These limitations have prompted efforts to develop alternative membranes for high temperature operation [16].

For the increasing energy efficiency and design of the fuel cell, proton exchange membranes are the key components. Thus, the researchers have focused to reach the proton exchange membrane with high proton conductivity, low electronic conductivity, and low permeability to fuel, low electroosmotic drag coefficient, good chemical/thermal stability, good mechanical properties and low cost [17]. In this area, N-substituted maleimide polymers are very useful and potent. N-substituted maleimides are known the most important class of the processable high-performance polymers. The other advantages of the N-substituted maleimides are high thermal stability, heat resistance and good mechanical properties [18-19]. Due to their thermal, electrical and high-temperature mechanical properties, these polymers have been used in many applications such as high temperature insulators, coatings, adhesives and matrices for high-performance composites [18-21]. In particular, different properties can be achieved by changing the N-substituent group onto the polymer chain. Therefore, recently, number of reports on the synthesis and polymerization of the N-substituted maleimides with different substituent groups have been published in many application areas [19-23]. But, N-substituent maleimide monomers with proton exchange groups have not been studied. The present paper reports the synthesis,

polymerization and microbial fuel cell application of N-[azobenzenesulfonic acid] maleimide as a proton exchange membrane. Obtained novel sulfonated poly(maleimide) has better thermal stability, high proton conductivity, easy processing, good mechanic and chemical properties. This sulfonated membrane composition is determined by elemental analysis, FTIR, NMR and thermal study was done with the help of DSC, DTA and TGA analysis. Prepared membrane has been tested for unit-cell performance in microbial fuel cell. We have especially investigated the possibility of stable sulfonated poly (maleimide) show some advantages as fuel cell membranes. The structure and some properties of the synthesized polymer were studied with particular emphasis on the PEM-related properties, such as proton conductivity, mechanical properties, water induced swelling, and stability of cast membranes.

## 2. EXPERIMENTAL

### 2.1. Materials and methods

All reactions were performed under inert atmosphere using standard Schlenck techniques. Solvents and chemicals were obtained from Aldrich and used as received unless specified otherwise. P-dimethylamino-azobenzenesulfonic acid (DMBSA) was used as received since the dye content was verified as to be 97%. An ultra-pure water filtering system was used to produce deionized water, and methanol was dried over calcium hydride.

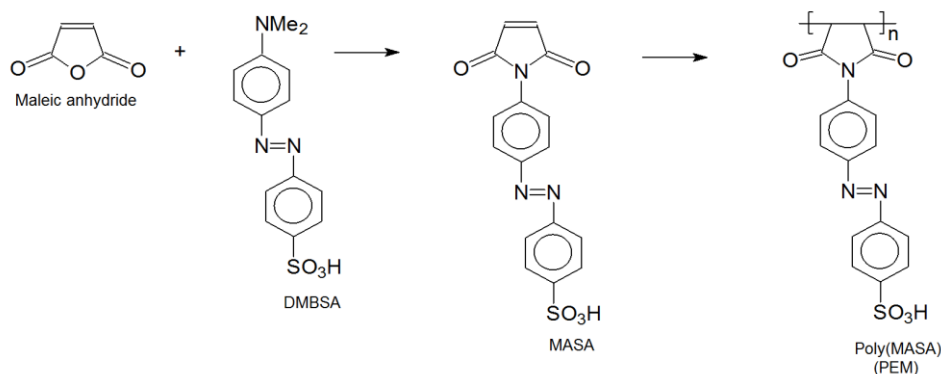
Infrared spectra were recorded as KBr pellets in the range 4000 - 400  $\text{cm}^{-1}$  on an ATI UNICAM systems 2000 Fourier transform spectrometer.  $^1\text{H}$  NMR spectra (300 MHz) on a Bruker AM 300 WB FT spectrometer with  $\delta$  referenced to residual solvent DMSO- $d_6$ . The thermal analysis (differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG)) were performed with Shimadzu, DSC-60, DTA-50 and TGA-50 thermal analyzers respectively.

Gel permeation chromatography (GPC) analyses were performed at 30  $^\circ\text{C}$  using N-methyl-2-pyrrolidone (NMP) as eluant at a flow rate of 0.5 mL/min. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system) was calibrated with a mixture of polystyrene standards (polysciences; molecular masses between 200-1200000 Da) using GPC software for the determination of the average molecular masses and the polydispersity of the samples.

### 2.2. Synthesis of PEM mebrane.

#### 2.2.1. Synthesis of the 4-maleimidoazobenzenesulfonic acid

4-Maleimidoazobenzenesulfonic acid (MASA) was prepared from maleic anhydride and *p*-dimethylamino-azobenzenesulfonic acid (DMBSA). The *p*-dimethylamino-azobenzenesulfonic acid (DMBSA) (5.50 mmol) and the required quantity of the maleic anhydride (5.50 mmol) and toluene (25 ml) were heated to 30  $^\circ\text{C}$  for 3 h. Then the mixture was refluxed for 18 h. The residual solvent was removed and the solid that obtain was washed with hexane and crystallized from toluene [24]. The yield was 81%. Elemental anal. calc. for  $\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_5\text{S}$ : (331.25): C: 53.39; H: 3.35; N: 8.46; found: C: 53.27; H: 3.09; N: 8.57.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm) 7.91 [s, 2H,  $\text{CH}=\text{CH}$ ]; 8.44 and 7.44 [d, 4H,  $J = 1.4$  Hz,  $\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{N}$ ]; 5.18 and 5.36 [d, 4H,  $J = 6.0$  Hz,  $\text{N}-\text{C}_6\text{H}_4-\text{SO}_3\text{H}-p$ ]; 2.01 [s, 1H,  $\text{C}_6\text{H}_4-\text{SO}_3\text{H}$ ]



Scheme 1: Synthesis of the sulfonated poly(maleimide) PEM mebrane.

### 2.2.2. Synthesis of the sulfonated poly(maleimide) PEM mebrane.

MASA (1.5 mmol) and benzoylperoxide (0.12 mmol) as an initiator were dissolved in 10 ml of toluene. The solution was poured into dry Schlenk tube and degassed twice by being purged with argon. The tube was closed and heated in an oil bath with stirring at 75 °C. The obtained polymer solution was slowly poured into 100 ml diethyl ether to precipitate the polymer. The precipitated polymer was collected by filtration and washed several times with an excess of hexane. The product was dried until the weight loss became essentially constant, 79% yield. Anal. calc. for (C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>5</sub>S)<sub>n</sub>: (331.25)<sub>n</sub>; C: 53.39; H: 3.35; N: 8.46; found: C: 53.27; H: 3.09; N: 8.57.

### 2.3. Membrane preparation

The sulfonated poly (maleimide) was dissolved in *m*-cresol to form about 5.0 wt% solutions. The membranes with a controlled thickness (dry membrane thickness: 50–80µm) were prepared by casting the solutions onto clean glass plates and were dried at 120 °C for 12 h. The membranes were carefully removed from the glass substrates using a sharp razor blade after they were cooled down to room temperature. The as-cast films were soaked in methanol at 60 °C for 1 h to remove the residual solvent and then were immersed in 1.5N hydrochloric acid at room temperature for 48 h for proton-exchange treatment. The membranes in acid form were thoroughly washed with deionized water and dried in vacuum at 120 °C overnight.

### 2.4. Determination of sulfonic acid concentration

The sulfonic acid concentration, i.e. sulfonation level or ion exchange capacity (IEC) of each sulfonated proton exchange composites membrane was determined by element analysis (EA). IEC of ion exchange polymers were usually determined by titration, but IEC measurement for sulfonated proton exchange composites membranes through titration method using strong base, 0.1N NaOH might cause to decompose sulfonated proton exchange composites membranes. Thus, from the weight of detected sulfur and carbon, the sulfonation levels were quantitatively evaluated by EA.

### 2.5. Fuel cell tests

Two-rectangular chambered MFCs (400 mL working volume; 25 mL headspace volume each) were constructed with a separation of sulfonated proton exchange membrane, 5 mm electrode spacing, and an external resistance of 100 Ω. The anode consisted of a carbon felt electrode (25 cm<sup>2</sup>). The cathode was made from 0.2 M a phosphate buffer with the same size as the anode, with 0.020 M potassium ferricyanide. The anode chamber was inoculated using aerobic biological fuel from the waste of sugar factory, and was filled with an autoclaved anaerobic nutrient mineral buffer (pH 7.0) solution, whereas the cathode chamber contained a phosphate buffer (pH 7.0) with continuous aeration. As substrate, glucose from the waste of sugar factory was used. Two MFCs with different bacteria (*Saccharomyces cerevisiae*, *haromyces cerevisiae* and *Enterobacter aerogenasa*) were operated with a gentle stirring in a temperature controlled room at 37 °C. Potential change was reported in biological fuel cells. The current voltage characteristics were recorded. The system was operated at ambient pressure.

## 3. RESULTS AND DISCUSSION

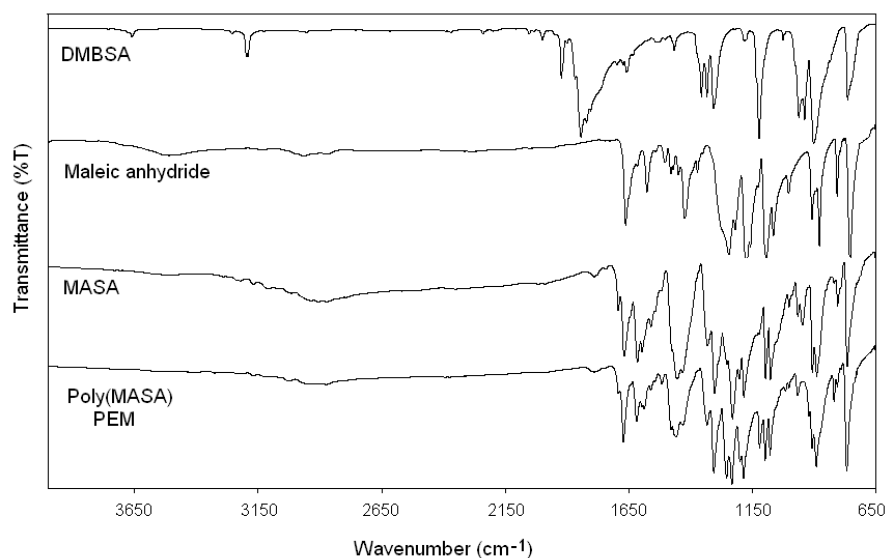
### 3.1. Membrane characterization

The structures of synthesized monomer and polymer as a proton exchange membrane were confirmed by FT-IR, elemental analysis and <sup>1</sup>H NMR spectroscopy in DMSO-d<sub>6</sub>. Variance of chemical structure during the polymerization reaction was identified by FTIR spectroscopy. FTIR spectra of maleic anhydride, DMBSA, monomer (MASA) and sulfonated poly(maleimide) (poly(MASA)) were shown in Figure 1. The peak at 1719 cm<sup>-1</sup> in FTIR spectrum of maleic anhydride was attributed to the C=O stretching vibration. After the reaction with the DMBSA, FT-IR spectra of monomer (MASA) revealed absorption bands ν(cm<sup>-1</sup>): 1601 cm<sup>-1</sup> (–N=N–); 1772 cm<sup>-1</sup>, 1710 cm<sup>-1</sup> (C=O symmetric and asymmetric stretch in a five member imide ring); 1523 cm<sup>-1</sup> (C=C from benzene); 829 cm<sup>-1</sup> (di-substitution of benzene); 1414 cm<sup>-1</sup> (C–N–C) and 1655 cm<sup>-1</sup>, 692 cm<sup>-1</sup> (C=C from maleimide ring). The imidization of the maleic anhydride to monomer (4-maleimidoazobenzenesulfonic acid) was confirmed by the disappearance of the aliphatic methyl peaks of the DMBSA structure at 2850-3100 cm<sup>-1</sup> and appearance of characteristic imide peaks at 1772 - 1710 cm<sup>-1</sup>. The FT-IR spectrum of poly(maleimide) obtained by the radical polymerization of 4-maleimidoazobenzenesulfonic acid indicated absorption peaks at 1774, 1704 cm<sup>-1</sup> (νC=O stretching of imide) (Fig. 1). For polymer as a proton exchange membrane, absorption of C=C within maleimide ring disappeared completely for the reason of polymerization to be finished. The FT-IR spectrum of the poly(maleimide) indicated characteristics absorption peaks at 1771 and 1705 cm<sup>-1</sup> (C=O

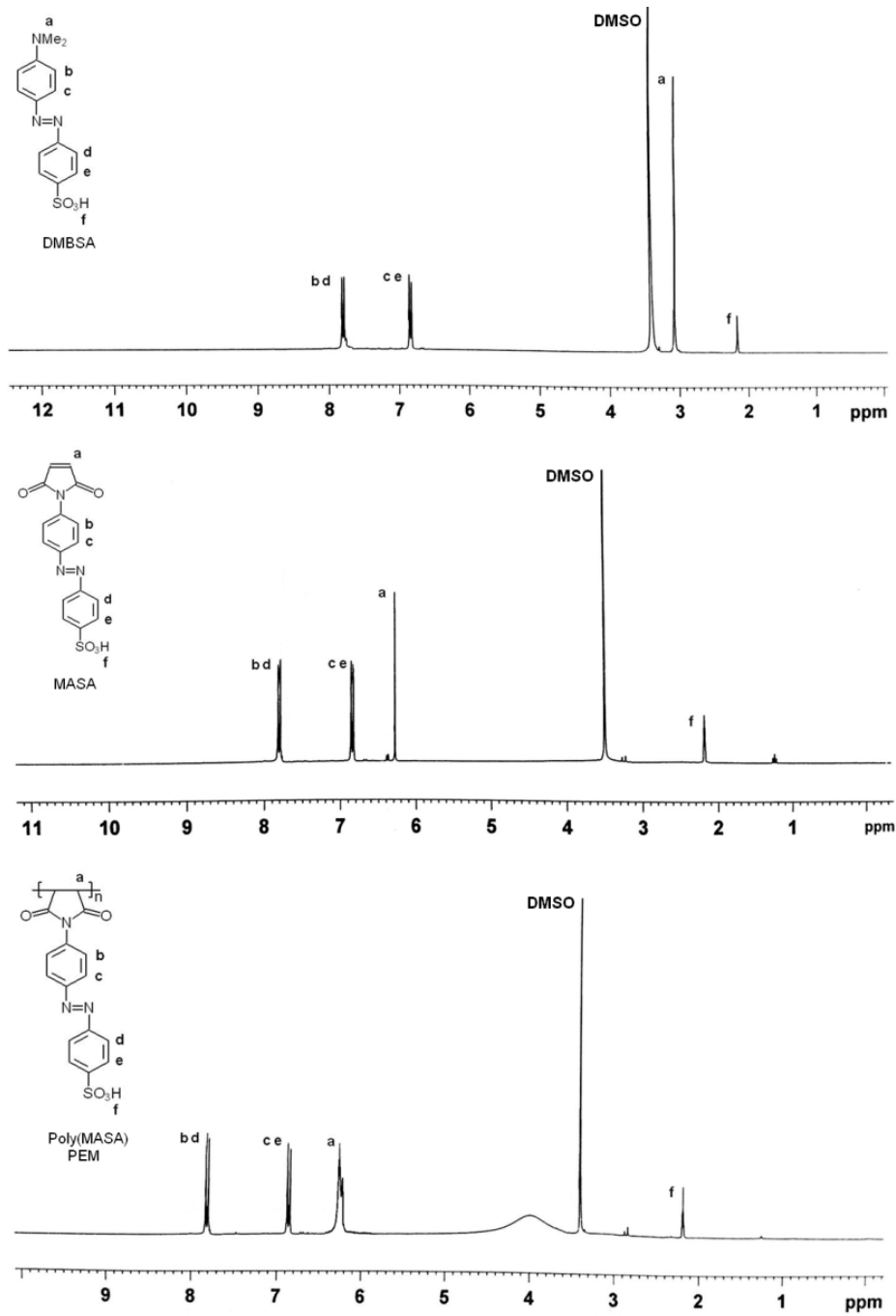
stretching) with the disappearance of vinyl absorption at  $1655\text{ cm}^{-1}$  that had appeared in the 4-maleimidoazobenzenesulfonic acid (MASA) [25-27].

The  $^1\text{H-NMR}$  spectrum of DMBSA, MASA and sulfonated poly(maleimide) were shown in Figure 2. The structure of the MASA was confirmed by the signal at 6,81-7,82 ppm due to aromatic phenyl ring and the signal at 2,12 ppm is attributed to the  $-\text{SO}_3\text{H}$  unit. Methyl peak that had appeared in the DMBSA at 3.03 ppm was not seen in the spectrum of the MASA.  $^1\text{H-NMR}$  spectrum also confirmed the formation of polymer. The  $^1\text{H NMR}$  spectrum of the sulfonated poly(maleimide) showed the disappearance of the vinyl absorption peak at 6.2 ppm, which was ascribed in the monomer (MASA). The elemental analyses of the 4-maleimidoazobenzenesulfonic acid and poly(maleimide) were in good agreement with the calculated values for the proposed structure.

The number average molecular weight ( $M_n$ ) determined by gel permeation chromatography (GPC) was 93000 for polymer. The polydispersity index ( $M_w/M_n$ ) of this polymer is close to about 1.85.

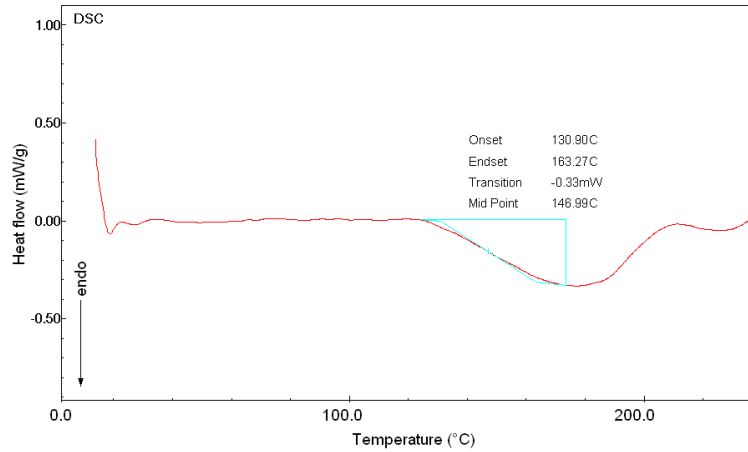


**Figure 1:** The FT-IR spectrum of the DMBSA, maleic anhydride, MASA and poly(MASA)

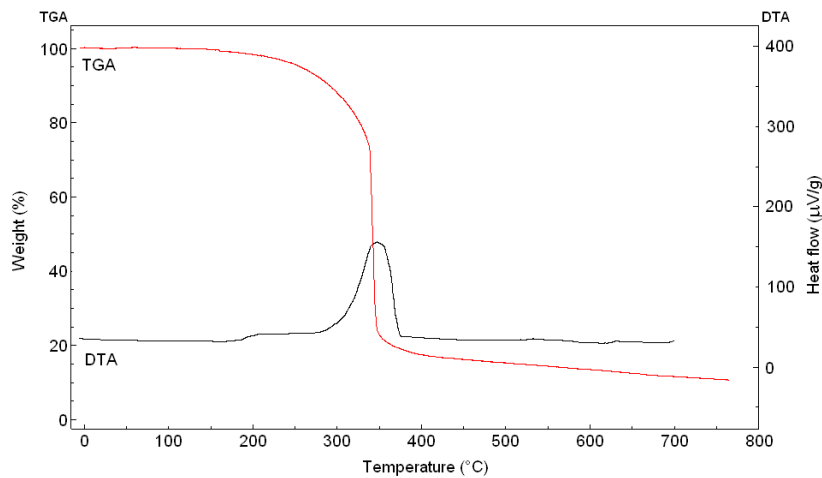


**Figure 2:** The NMR spectrum of the DMBSA, MASA and poly(MASA)

DSC curves of the polymers showed the glass transition temperature ( $T_g$ ) 147 °C for The sulfonated poly(maleimide) (Fig. 3). The exothermic transitions were observed in differential thermal analysis (DTA). The complete weight loss occurred above 394 °C evidenced by TGA (Fig. 4.)



**Figure 3:** The DSC curve of the sulfonated poly (maleimide) (scan rate 10 °C/min).



**Figure 4:** The TGA and DTA curves of the sulfonated poly(maleimide)

### 3.2. Determination of sulfonic acid concentration

The actual sulfonation level as a function of designed sulfonation level is 15,2 (mol%) and ion exchange capacity is 0,56 mmol/g. Thus, the membrane with the targeted sulfonation level was easily achieved by adjusting the molar ratio of monomers.

### 3.3. Fuel cell performance

The performance of the membrane in fuel cell was characterized in the permeation device and described. Course of voltage during short-term testing of sulfonated proton exchange composites membranes in constant current (1 A) mode are shown Fig. 5. The cell was run for 24 h each bacteria at 37 °C in constant current (1 A) mode without any marked loss in performance.

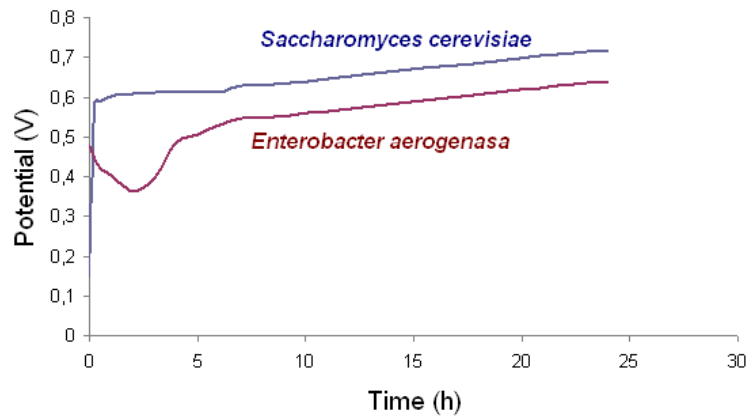


Figure 5. Microbial fuel cell performance of the sulfonated poly (maleimide) membrane.

### 3.4. Effect of temperature

Fig. 6 shows the polarization curves obtained by changing the external load at several temperatures. Good performance was observed in the range of 30 °C to 42 °C with the highest yield at 37 °C, the optimum temperature for *Saccharomyces cerevisiae* growth. At temperatures higher or lower than 37 °C, the cell could not pass sufficiently large current. Below ca. 1 mA, the cell voltage did not show sensitive change with temperature, but above 1 mA the operation at 37 °C showed much better characteristics. This result is related to the enzymatic activities within *Saccharomyces cerevisiae*. At optimum temperature, enzymes display maximum activities, leading to the highest metabolic rate.

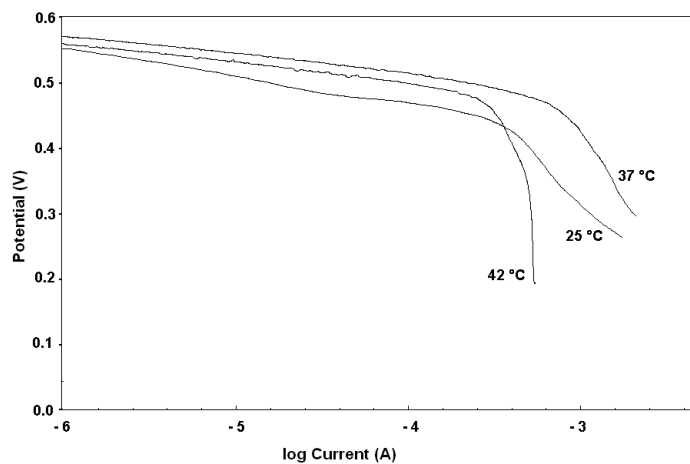


Figure 6. Polarization curves for the fuel cell *Saccharomyces cerevisiae* at 25 °C, 37 °C and 42 °C



#### 4. CONCLUSIONS

In this paper, We have especially investigated the possibility of stable sulfonated poly (maleimide) show some advantages as fuel cell membranes. The structure and some properties of the synthesized polymer were studied with particular emphasis on the PEM-related properties, such as proton conductivity, mechanical properties, water induced swelling, and stability of cast membranes. We developed a prototype microbial fuel cell using microorganisms tested its performance under various conditions. *Saccharomyces cerevisiae* or *Enterobacter aerogenasa* and the waste of sugar factory were placed in an anodic compartment, and our cell was able to produce electricity.

#### 5. REFERENCES

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