Microbial Fuel Cell Performance Enhancement through Modification of Nafion Membrane Using Sulfuric Acid-Doped Polyaniline

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Abstract

In the face of dwindling energy resources and the alarming surge in harmful greenhouse gas emissions, there is a crucial shift towards embracing renewable energy solutions that minimize environmental impact. For this goal, Microbial Fuel Cells (MFCs) are used as a dual-purpose technology; functioning potentially as great energy generators and environmental cleansers. This study delves into the enhancement of MFCs' efficiency through the customization of the Nafion proton exchange membrane using sulfuric acid-doped polyaniline. Due to this quality, Polyaniline was selected for its robustness and high electrical conductivity. Later, it was electrochemically deposited onto the Nafion membrane, employing a method rooted in electrochemistry. Experimental trials involved a dual-chamber MFC, employing Escherichia coli and glucose as substrates. Assessing the Nafion membrane's condition using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR), the MFC with the modified Nafion membrane exhibited significantly higher maximum current density (285 mA/cm^2) and power density (36 mW/cm^2) compared to its pristine Nafion counterpart; titled (165 mA/cm^2) and (14.5 mW/cm^2) respectively. A comparison with the polarization curve displays an improvement in the microbial fuel cell's performance attributed to the Nafion membrane modification.

Keyword: Microbial Fuel Cell, Nafion, polyaniline, Sulfuric Acid, environmental

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1- Introduction

The primary sources of energy employed in today's industrial world are derived from renewable fuels including various hydrocarbon materials (1). The increasing daily consumption of fossil fuels for energy supply has led to the emission of carbon dioxide and greenhouse effects (2, 3). Ongoing research aims to gradually replace and utilize renewable energy sources including geothermal, hydropower, nuclear radiation, solar energy, ocean (tidal and wave) and bioenergy production (3-5). Microbial fuel cells represent one of the latest developments in the field of renewable energy (6).

A MFC comprises a proton exchange membrane, anode and cathode chambers, electrodes and microorganisms (1, 7, 8). Any biodegradable and oxidizable substance can serve as a substrate in MFCs for microorganisms. Therefore, a wide range of materials and pollutants can be utilized as energy sources in MFCs (9).

Electricity generation through the activity of microbial biocatalysts is a result of the anaerobic oxidation of substrates by microorganisms (bacteria) converting chemical energy into electrical energy (6, 7). The proton exchange membrane is one of the most crucial components of MFCs. An effective proton exchange membrane should possess properties such as high conductivity, low internal resistance (10) and selective proton permeability (4).

Electrons and protons generated from the oxidation of substrates in the anode chamber enter the cathode chamber through an external circuit and the proton exchange membrane and ultimately, they combine with oxygen to form water molecules. This ion transfer besides producing electricity (4, 6, 7) maintains the cell in a neutral state (11, 12).

Nafion proton exchange membrane facilitates proton transport through negative groups such as sulfonic acid (SO_3H) (13-15). Among various conductive polymers, polyaniline is preferred due to its excellent conductivity, ease of synthesis and cost-effectiveness (6, 16).

2- Experimental Section

2-1- Vacuum Distillation of Aniline

Aniline must be used in a pure form without oxidizing agents. Therefore, vacuum distillation was initially employed to achieve this. Vacuum distillation is utilized to minimize heat exposure preventing damage to aniline. Using this method, the boiling point of aniline which is 184°C is reduced to 70°C.

2-2- Pretreatment of Nafion Membrane

The Nafion 112 membrane must undergo pre-treatment before being used in a microbial fuel cell. This process is done in four stages:

- Washing with H_2O_2
- Rinsing with distilled water
- Washing with H_2SO_4 (1M)
- Final rinse with distilled water

Initially, a piece of Nafion 112 film is cut according to the size of the MFC. Subsequently, pretreatment is conducted according to the aforementioned stages. Each stage is carried out at a temperature of 80°C for one hour (17-19).

2-3- Electrochemical Polymerization of Aniline on Nafion Membrane

The aniline polymerization is done through the electrochemical method. Initially, aniline was distilled, and sulfuric acid was mixed to dope aniline. Afterwards, the pre-treated Nafion membrane was put in an aniline and sulfuric acid mixture. In the fourth stage, the electrochemical polymerization of aniline on the surface of the Nafion membrane was carried out to form doped poly-aniline on the Nafion membrane.
To increase the potential of the electrochemical polymerization of doped aniline with, sulfuric acid on the Nafion membrane, A power source was used. The color of the Nafion membrane changed from transparent to black.

2-4- Microbial Fuel Cell (MFC)

The MFC used in this experiment consisted of two chambers. Graphite served as the electrode in both the anode and cathode chambers. The Nafion membrane was employed as a separator between the anode and cathode chambers and as a proton transporter. The anode chamber was filled with Escherichia coli microorganisms. The generated current and voltage values from the MFC were measured using a digital voltmeter connected to the external circuit and then recorded. Fig.1 shows the changes in the anode chamber at the start and end of the MFC operation.

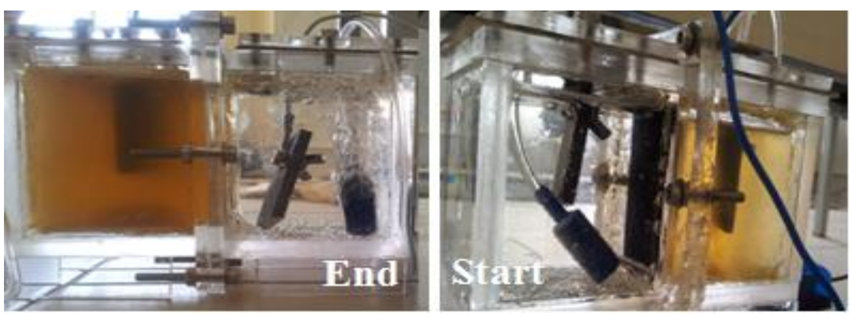

Fig.1 changes in the anode chamber at the start and end of the MFC operation

3- Results and Discussion

3-1- MFC Polarization Curve

The polarization curves of the microbial fuel cell are plotted in Fig.2. This graph depicts variations in voltage and power density against current density providing insights into the performance of the MFC. The assessment of microbial fuel cell performance is primarily done through the trend of voltage, power density, and current density changes. The ascending trend in the slope of the performance curve indicates a favourable performance of the microbial fuel cell. The MFC with the Nafion membrane modified by doped polyaniline with sulfate exhibits significantly higher current and power density compared to the MFC with the unmodified Nafion membrane.

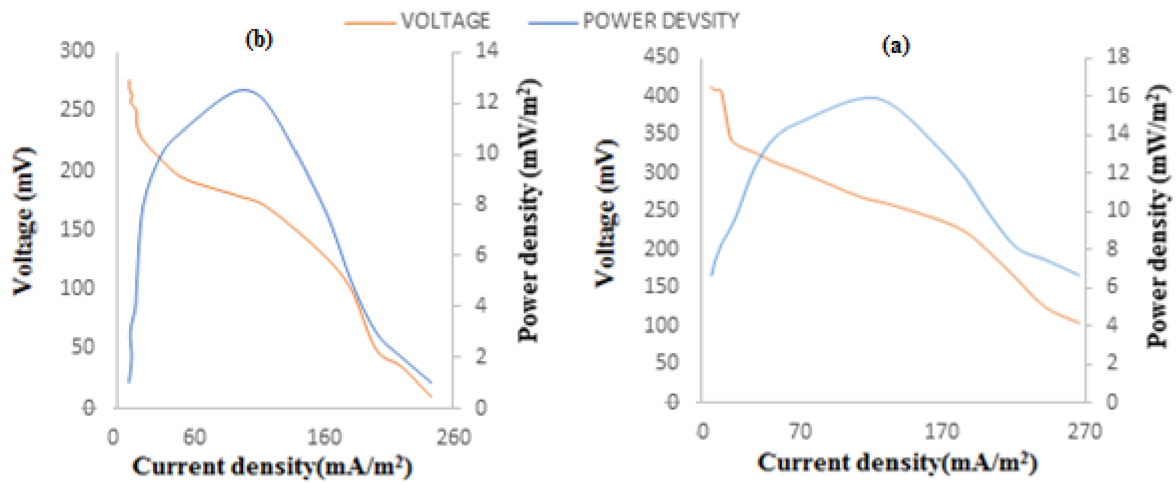

Fig.2 MFC polarization curve; a) with Nafion membrane modified with H_2SO_4-doped polyaniline and b) with unmodified Nafion membrane

3-2- Power Density Change Comparison

Fig.3 represents the change in power density during six measurement stages throughout the experiment using various Nafion membranes.

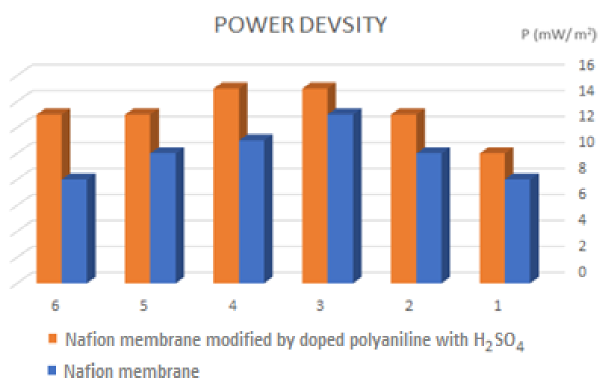

Fig.3 Power density change (mW/m^2)

According to the graph, the power density is increasing. In comparison, the Nafion membrane modified with sulfonated polyaniline shows the best trend.

3-4- Current Density Change Comparison

Fig. 4 displays the change in current density during six measurement stages throughout the experiment using different Nafion membranes.

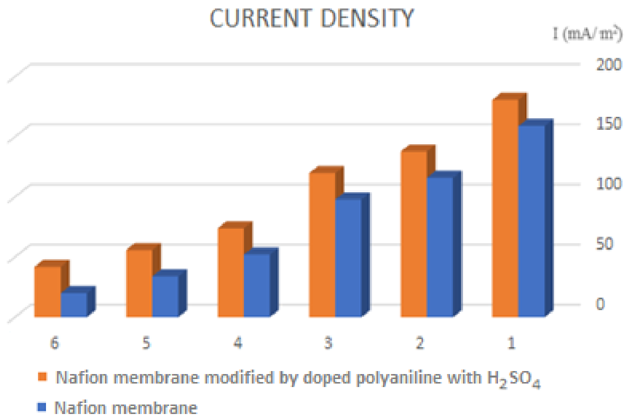

Fig.4 Current density change (mA/m^2)

Considering the values in the graph, representing the generated current in the device, the trend of increasing current density is evident. The presence of polyaniline contributes to an effective increase in current and current density. The best condition is observed in the Nafion membrane modified with sulfonated polyaniline.

3-5- Characterization

Scanning Electron Microscopy (SEM) imaging was employed to visualize the surface of the Nafion membrane modified by doped polyaniline as shown in Fig. 5. The presence of polyaniline on the Nafion membrane is evident in the images.

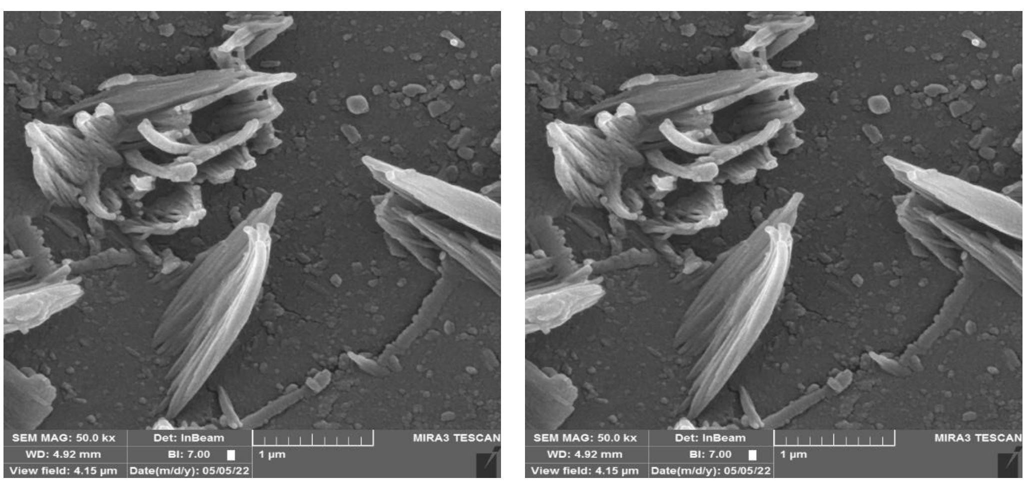

Fig. 5 Sulfuric Acid-Doped Polyaniline on the Surface of the Nafion Membrane

Fig. 6 presents the FTIR test for the Nafion membrane modified by aniline doped with sulfuric acid. Vibrational stretching for the asymmetric mode of the O=S=O group is observed in the region of 1214 cm^{-1}. The vibrational bending for the S-O group is seen in the region 1048 cm^{-1} (20, 21). The region 1579 cm^{-1} and 1489 cm^{-1} are attributed to the stretching vibrations of N=C and C=C bonds in polyaniline respectively. The region 1300 cm^{-1} corresponds to the bending vibration of N-H and may also be related to the stretching vibration of protonated C-N. The stretching vibration related to the C-S bond is found at 1598 cm^{-1}. Vibrational stretching of N-H and O-H is indicated at 3120 cm^{-1} (22). The bending vibration associated with the benzene ring's C-H bond is at 506 cm^{-1}. Additionally, stretching vibrations of the C=O bond is observed at 1700 cm^{-1} (23). The asymmetric stretching of CF_2 is at 1199 cm^{-1}, symmetric stretching of CF2 at 1144 cm^{-1} and asymmetric stretching of $SO3^-$ in the region 1057 cm^{-1} for the Nafion membrane.

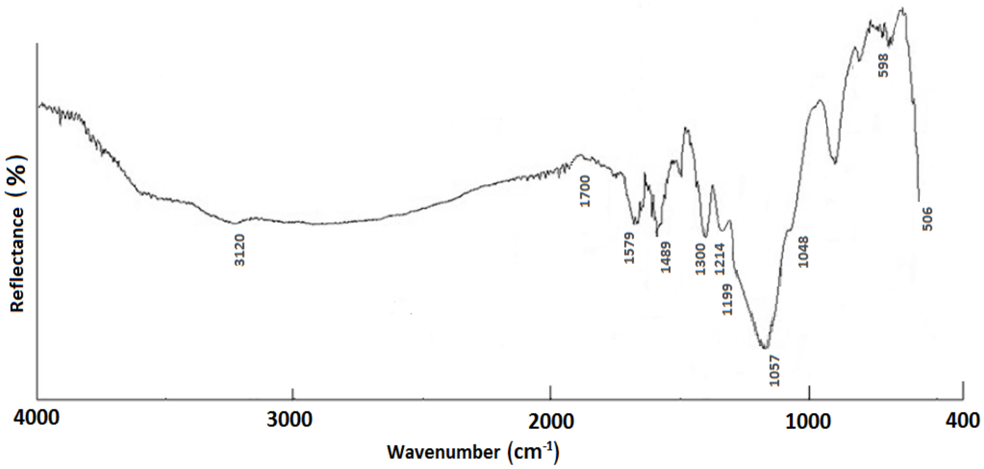

Fig. 6 FTIR spectrum of Nafion modified with sulfuric acid-doped aniline

4- Conclusion

Polyaniline, as a conductive polymer, has gained attention due to its low cost, easy preparation, high nitrogen content, and polar functional groups (24). For the electrochemical polymerization of aniline on the Nafion membrane, H_2SO_4 was used as a ligand. SEM and FTIR tests, conducted to investigate the structure and surface of the membrane, indicated that aniline was polymerized on the surface of the Nafion membrane.

The slope of the polarization curve reflects the internal resistance and performance of the microbial fuel cell (25, 26), and showed an improved performance of the microbial fuel cell with the Nafion membrane polyaniline modified (doped with H_2SO_4). This enhancement can be attributed to the hydrophobic nature of the Nafion membrane (28, 27, 14), multiple properties, and conductivity of polyaniline (29). The interaction between sulfonic acid groups in the Nafion matrix and polyaniline has increased proton conductivity. On the other hand, water molecules play the role of bridges between ionic branches, connecting one ionic branch to another, facilitating the rapid proton transfer and increasing conductivity in the Nafion proton exchange membrane (27).

The presence of sulfuric acid with the (SO_3) group provides more space and a higher amount of proton transfer in the Nafion membrane. Considering the values of current density and power density, the efficiency of the microbial fuel cell with the Nafion membrane modified with polyaniline (doped with sulfuric acid) is significantly higher than microbial fuel cells with a conventional Nafion membrane.

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