Potential of PVDF Modified with Acidic Zeolite-Y Mix Matrix Membranes for Microbial Fuel Cell Application

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**Abstract.** Microbial Fuel Cells (MFCs) are biotechnologies that promise electrical energies from microbial activity. This activity used microorganisms as an oxidation agent for organic compounds and also produced electrons and protons as the side products. One of the components in MFC should have protons transport material from the cathode to anode to keep the reaction in the steady-state condition. Membrane materials in MFC support protons’ movement in the mechanism of Proton Exchange Membrane (PEM). Therefore, this research developed the mix matrix membranes (MMMs) PVDF and the addition of Zeolite-Y as a filler modified by acid to increase the proton's permeability performance. Modified zeolite and membranes were characterized by XRD for identification the crystalline structure and water contact angle (WCA) for identification the membrane hydrophilicity. Fuel cell performance was analyzed by measurement of voltage and current then calculation the power density in 3 hours. Modification in membrane shows a potential material for PEM mechanism in MFC applications.

# Keywords: Acidic Zeolite-Y, Microbial Fuel Cell, Proton Exchange Membrane, PVDF Membrane

## INTRODUCTION

The increased amount of fossil fuel needed in the world has a great impact on the increase in CO2 gas emissions. As reported by the G20 conference, the emissions of CO2 reached up to 35 billion tons [1]. However, net zero emissions in 2050 will target decrease in CO2 in the environment to 80%. Recent developments in biotechnology have the potential to generate renewable, energy. Microbial Fuel Cell (MFC) was a biological reactor to produce electric energy by microorganisms such as bacteria. Microorganisms in MFCs play a major role as biocatalysts in the oxidation reactions at the anode. In addition to generating electrical energy, MFCs can also treat wastewater and heavy metal waste [2].

Another component with a major role in the MFC is the material that separates the anode and cathode sides. These two sides are separated by a proton exchange membrane (PEM) [3–5]. Energy formed by an oxidation reaction at the anaerobic anode side, in which protons and electrons were formed. Electrons are transferred to the cathode side by the electrode, and protons are transferred to the cathode side by the PEM [6–8]. The cathode as an acceptor of protons and electrons was followed by the chemical equation below.

Anodic Reaction: CH3COOH + H2O → 2CO2 + 8H+ + 8e-

Cathodic Reaction: 8H+ + 8e- + 2O2 → 4H2O

Overall Reaction: CH3COOH + 2O2 → 2H2O + 2CO2

Thus, these reactions generate voltages because of the potential differential between the electron acceptor in the cathode and the oxidation reaction in the anode [9,10]. One factor that influences the voltage is the protons permeability of the membrane [11]. The selection of membrane materials was an important aspect of the synthesis of PEM. Membrane materials should have a good mechanical strength and hydrophilic; also, membranes should have good protons permeability [11]. Poly(vinylidene fluoride) (PVDF) is membrane polymer that has many advantages, as easy to fabrication and good stability in chemical and physical properties [12,13]. The PVDF membrane was fabricated by dry-wet phase inversion method to form flat sheet, hollow fiber, and tubular membranes. However, PVDF membranes have limited applications in PEM. The membrane’s pore size could permeate the water. PEM was not allowed to permeate the water because microorganisms in the anode and water in the anode could be mixed. In addition, PVDF is a hydrophobic membrane. The hydrophobic side of the membrane affects the decreased MFC performance. Hence, the modification of the PVDF membrane is needed to increase its hydrophilicity properties [14].

Zeolite-Y is an aluminosilicate material that is usually used as a filler in the membrane matrix to form mixed matrix membranes (MMMs) because it is compatible with the membrane matrix. In addition, several studies reported that adding zeolite-Y as a filler could reduce the pore size of the membrane. Hence, PVDF/Zeolite-Y was potentially used as a PEM in an MFC reactor. The hydrophilicity properties of PVDF membranes could be increased by modifying filler with an acid solution. The activation of the filler was aimed as ion exchange with H+ from the acid [15]. In this work, filler was activated with zeolite with variation of concentrations of 1, 2, and 3 M. MMMs and filler were characterized by XRD to identify crystalline structures, then water contact angle (WCA) to identify hydrophilicity properties in each variation of MMMs. Then, membrane performance was tested in an MFC reactor with *Bacterium strain* BS2049 as bacteria on the anode side. The voltage and current were measured every three hours. The power density was then calculated to identify the membrane performance.

## EXPERIMENTAL

## Materials

Poly(vinylidene fluoride) (PVDF), n-methyl pyrrolidone (NMP), chloride acid (HCl, 37%), Zeolite Y commecial, ammonium chloride (NH4Cl), potassium chloride (KCl) monosodium phosphate (NaH2PO4.2H2O), disodium phosphate (NaHPO4.H2O), and Nutrient Broth (NB).

## Filler Preparation

The 5 grams of commercial Zeolite-Y dissolved in 100 mL HCl solution. The solution was then stirred for 16 hours at room temperature. The zeolite then washed with aquadest until reach pH 5 – 7 and dried in oven 60-80 °C overnight. Variations in the concentration of acid solutions 1 M, 2 M, and 3 M. Activated zeolite by AZX, where X refers to the variation in acid concentration.

## Mix Matrix Membrane Fabrication

The fabrication of MMMs used the dry-wet phase inversion. The dope solution (400 grams) prepared with the ratio of PVDF/NMP was 16/84 %w. 1% wt of AZ dispersed into NMP solvent and then sonicated in 15 minutes. Then, the PVDF powder was added and the dope solution was stirred at 400 rpm in 80 °C for 24 hours. The dope solution was then let overnight to remove the bubbles then cast on glass plate to fabricate the MMM. Glass plate then soak in the non-solvent solution including water and ethanol in ratio 3:1 for 3 hours to remove the solution. The MMM dried in room temperature for 2-3 days until it dry.

## Characterization

Identification of crystal structure in each variation of AZ has been done by X-Ray Diffraction (XRD) characterization. The X light absorbed by the materials will be scattered and make a diffractogram according to its crystal structure. The hydrophilicity of the membrane measured by Water Contact Angle (WCA) by dropped a water into MMM’s surface. Membranes are classified as hydrophilic when the contact angle is less than 90.

## Fuel Cell Performance Test

Fuel Cell Performance Test analyzed by double chamber MFC reactor included the bacteria in anode side, electrolyte solution in cathode side and carbon as electrode connected by multimeter. The bacteria cultured with inoculation of *Bacterium strain* BS2049 in 10 mL of steriled Nutrient Broth (NB). The bacteria then incubated for 24 hours. Then, the optical density (OD) measured using UV-Vis Spectrophotometer in wavelength of 600 nm. The electrolyte solution made by dissolved 0,31 g NH4Cl, 0,13 g KCl, 4,97 g NaH2PO4, and 2,75 g Na2HPO4 with aqua DM in 1000 mL volumetric flask. The MMMs paired between the reactor as separator of anode and cathode solution. Current and voltage measured by multimeter for three hours and analyzed the power density calculation below.

Power Density (W/m2) =

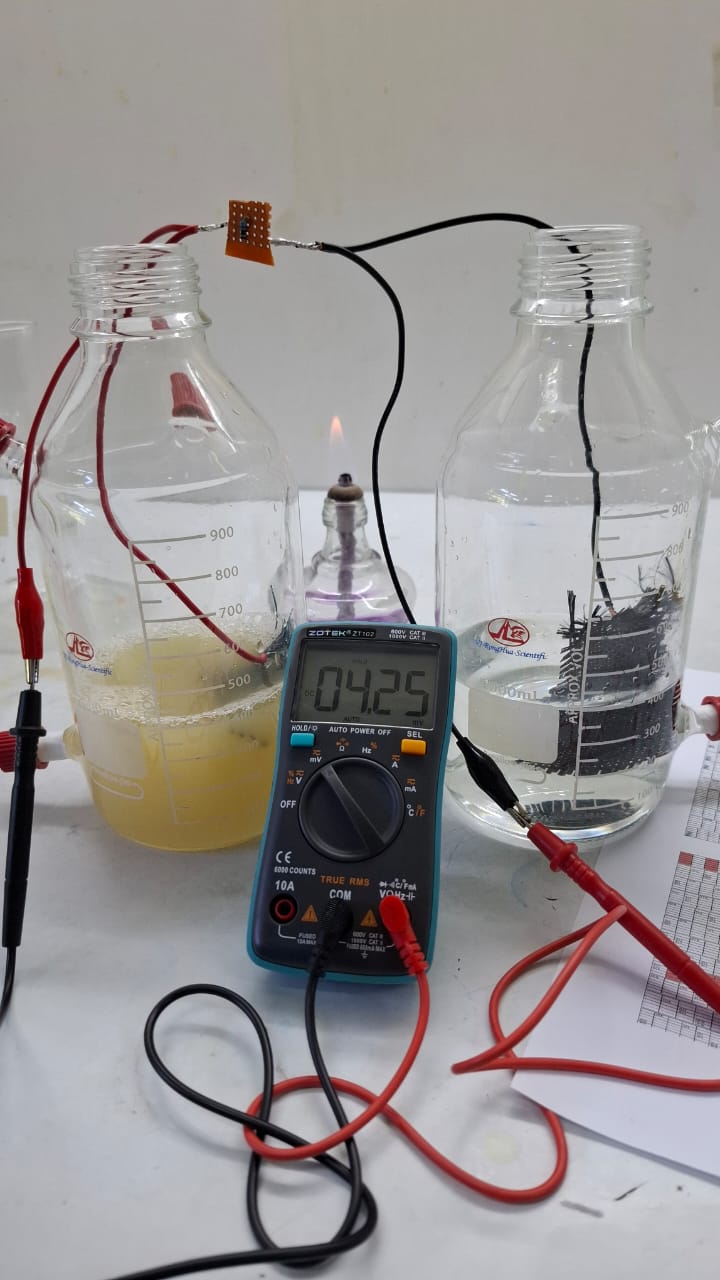
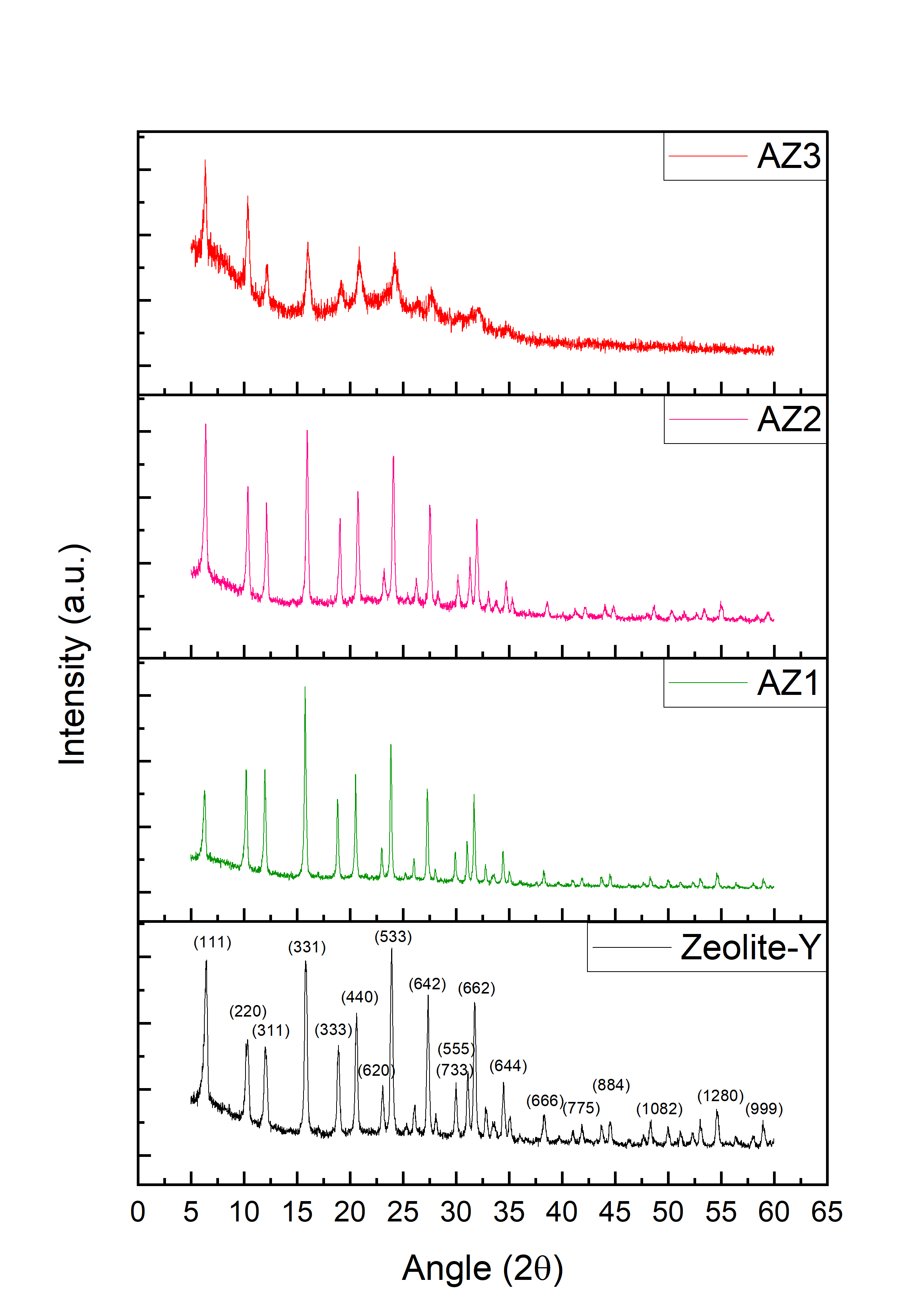


Fig 1. Fuel Cell Performance Test used MFC Double Chamber Reactor

## RESULTS

## XRD Analysis

The diffractogram of Zeolite-Y shows characteristic peaks at 2θ = 6.2°, 10.3°, 11.9°, 15.8°, 18.9°, 20.8°, 24.0°, 27.4°, and 31.4°, which are consistent with the standard pattern of Zeolite-Y. After acid activation, the samples (AZ1–AZ3) still exhibited the main reflections of Zeolite-Y, indicating that the crystalline framework was largely preserved. However, the intensity of the peaks decreased as the acid concentration increased. In particular, AZ3 displayed much broader and weaker peaks, suggesting partial loss of crystallinity and a tendency toward amorphization. This change reflects structural damage to the zeolite framework caused by excessive dealumination during strong acid treatment, as also reported in previous studies [16], [17,18].

``Fig. 2 XRD Difrractogram of Commercial Zeolite-Y and Activated Zolite-Y

## WCA Measurement

A graph of water contact angles

Description automatically generated

Fig. 3 Water Contact Angle Measure Results

According to graphic in Fig 3, the PVDF membrane showed the hydrophobic properties. After adding AZ as filler, the contact angle decreased up to 31.17% showed the higher hydrophilicity properties in MMM. By adding more filler could not increase the hydrophilicity properties significantly. It showed in PVDF/AZ3 variation that the hydrophilicity properties increased only 2.16% compared to PVDF/AZ2. The increased of hydrophilicity properties after AZ was added into membrane caused by a hydrogen bond between Si-OH in AZ and water occur because of acid activated in zeolite [17].

## Fuel Cell Performance

The ability membrane in MFC application showed by power density calculation in each variation of membrane. The power density calculated from current and voltage measurement using multimeter. Current and voltage measured for 3 hours, where the data collected in every one hour. The voltage generated for each membrane shows an increase. The highest voltage increase occurs in the AZ3 membrane variation. However, there was a significant voltage decrease in the third hour. This is due to the damaged structure of the filler material referring to the results of the XRD diffractogram. Damage of the filler material results in imperfections in the displacement of protons passing through the membrane. This is supported by other membrane variations that show that there is no significant trend. The variations of the AZ1 membrane and the PVDF membrane do not show a significant increase in current. This is because the acidity concentration used in zeolite activation is not enough to improve the performance of the membrane in proton transfer. The current generated on the AZ3 membrane has increases in the first hour and continues to be constant until the third hour. As for the AZ2 membrane, there was a very sharp decrease in the first hour and then an increase in the third hour. This change in current occurs due to the resulting resistance for each variation. However, there was an increase in current between the membrane and the acid-activated zeolite filler and the neat PVDF membrane.

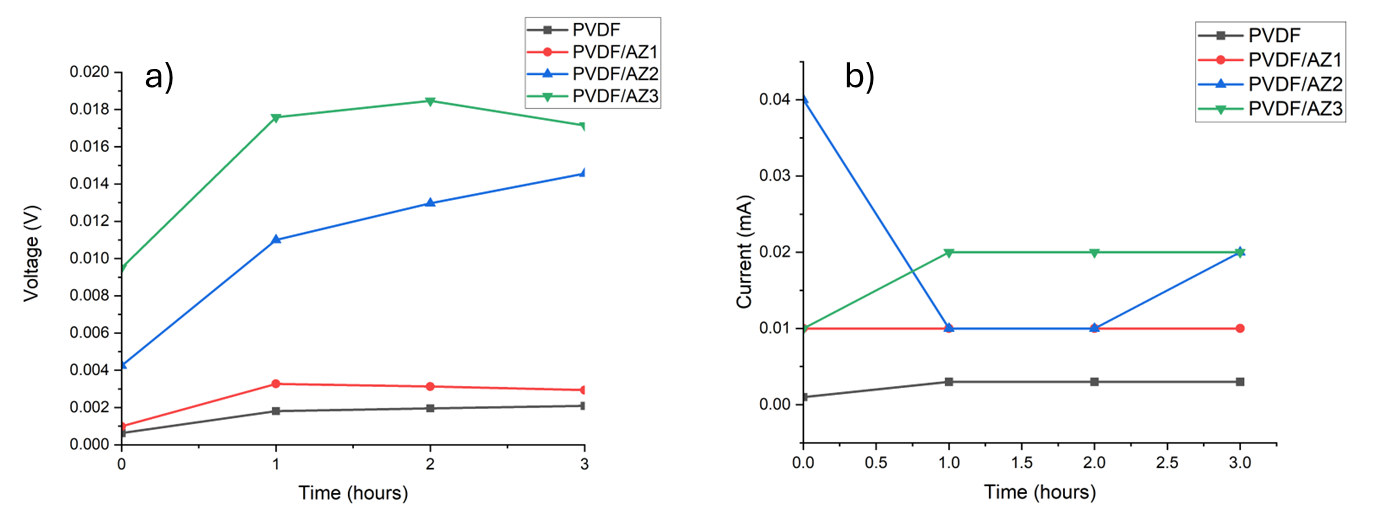


Fig. 4 Voltage (a) and Current (b) Measured for 3 Hours

The power density results are shown in Figure 4. The neat PVDF membrane gave the lowest value and stayed almost flat at around 0.01 mW/m² during the whole test. This is expected because PVDF is hydrophobic and does not support good ion transport. When acid-activated zeolite was added, the power density increased. The PVDF/AZ1 membrane showed a small improvement compared to neat PVDF but was still low. The PVDF/AZ2 and PVDF/AZ3 membranes showed much higher values. The highest result was from PVDF/AZ3, reaching about 0.09 mW/m² after 2 hours, although it decreased slightly at 3 hours. PVDF/AZ2 first decreased, then increased again in the third hour, which shows the system needed time to stabilize. The improvement comes from the hydrophilic groups and pore structure of the acid-activated zeolite, which make it easier for ions to move through the membrane. But too much activation, as in AZ3, can damage the structure and affect stability, which may explain the drop at 3 hours. From these results it can be seen that adding acid-activated zeolite clearly improved the power density compared to neat PVDF. The best stability was found in PVDF/AZ2, while the highest value was reached by PVDF/AZ3.

A graph of different colored lines

AI-generated content may be incorrect.

Fig 5. Power Density for Each Membrane

## CONCLUSION

Based on the results of the research that has been carried out, acid-activated PVDF/Zeolite-Y MMMs have been successfully synthesized. Acid-activated Zeolite-Y filler materials have been characterized and exhibit characteristics that affect membrane performance in proton transfer. The use of high concentrations of acids can damage the crystal structure of zeolite as evidenced by the results of XRD difractograms. In addition, an increase in acid concentration can also increase the hydrophilicity of PVDF membranes. The results of the Fuel Cell performance test show that acid-activated PVDF/Zeolite-Y membrane can increase the voltage, current, and power density of the MFC process.

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