Active Natural Zeolite Utilization for Microbial Fuel Cell
Membrane Modification

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Abstract. Microbial fuel cell (MFC) consists of anode and cathode separated by proton exchange membrane (PEM). Effectivity of MFC system determined by the conductivity of PEM which can be enhanced active porous material addition such as natural zeolite that attract proton. The activation of natural zeolite is carried out with acidification method. Active zeolite particle used in this project is 437 nm in diameter. The active zeolite is used as filler to increase ionic conductivity of sulfonated polyether-ether ketones (sPEEK) with variation of 1%, 3%, 5%. The ionic conductivity of sPEEK-active zeolite electrolyte membrane is approximately $1.25 \times 10^{-2} - 2.8 \times 10^{-2}$ S/cm. Accordingly, this electrolyte membrane is potential for MFC application.

Keywords: active natural zeolite; ionic conductivity; microbial fuel cell; proton exchange membrane.

1 Introduction

Mohan, et al [1] and Liu, et al [2] have reported that microbial fuel cell (MFC) is the one of utilities which can be recover renewable energy from waste organic sources. Sun et al [3] have studied many substrates of waste organic sources which can be used in MFC system for electricity production. However, microbial fuel cell faces limitations in terms of development to large scale application. Research conducts to the microbial fuel cell technology development which is more economically feasible and applicable should focus on reactor configuration, power density and the material costs according to Pham et al [4].

The design of common MFC requires the separation between anode and cathode, the name of this compartment is PEM (Proton Exchange Membrane).
Tsuchiya et al [5] have said that proton exchange membrane (PEM), which is used in MFC, represents a cost to be focused. The most commonly PEM that we used in MFC system is Nafion (Dupont Co., USA), which is available from numerous suppliers (e.g., Aldrich and Ion Power, Inc.). Rabaey et al [6] have reported that Ultrex CMI-7000 (Membranes International Incorp., Glen Rock, NJ) are well suited for MFC application also beside Nafion. This membrane are considerably more cost-effective than Nafion.

When a PEM is used in an MFC, it is important to recognize that it may be permeable to chemicals such as oxygen, ferricyanide, other ions, or organic matter used as substrates. The market for ion exchange membranes is constantly growing, and more systematic studies are necessary to evaluate the effect of the membrane on performance and long-term stability. Lufrano et al [7], Rikukawa et al [8], Nunes et al [9], and Robertson et al [10] have studied MFC membrane alternatives which have been developed from various hydrocarbon polymers, such as polysulphone, poly benzimidazole, polyether-ether ketones.

In Indonesia, zeolite research and development for various purpose is still underway. Arifin et al [11] have reported based on data from the Assessment and Development Center of Mineral Technology, investigation of zeolite in Indonesia has begun in the 1980s. Deposit of zeolite in Indonesia is approximately 206.42 million tonnes in the island of Java, Sumatra, Kalimantan, Maluku and Sulawesi. In this research, properties of zeolite as adsorber will be used to modify electrolyte membrane in MFC system. Arimura [12], Arico [13], and Domitrova [14] have studied that inorganic additives in the electrolyte membrane will increase their ionic conductivity.

2 Methods

2.1 Natural Zeolite Activation

Natural zeolites from Gunung Kidul area are crushed and sieved in a 200 mesh sieve equipment. Approximately 100 grams of 200 mesh zeolites are soaked in 37 % Hydrochloric acid (HCl) solution and have been refluxed for 2 hours. After that, zeolites were allowed in the room temperature condition until formed into two layers. The top layer was removed and zeolites were washed using distilled water by flushing distilled water on a Buchner filter for several times. The next step is zeolites were added by 33 % NH₃ solution and were refluxed for 2 hours.
After that, zeolites were allowed in the room temperature condition until formed into two layers. The top layer was removed and zeolites were washed using distilled water by the same way as before. Washing process was done until the pH netral (it is marked by red litmus paper which does not change when dipped into filtrate of zeolites washing). Zeolites were heated in 120 °C for 4 hours.

2.2 Active Natural Zeolites Characterization

Active natural zeolites particles were characterized by Particle Size Analyzer (PSA) equipment (Beckman Coulter Delsa Nano).

2.3 Sulfonation and Electrolyte Membrane Preparation

Poly ether ether ketones (PEEK) sulfonation process is reacting PEEK with sulphuric acid (96-98 %) in the ratio of 1 : 20 (w/v). To get more appropriate reaction, they were stirred. Temperature was set around 60 °C for 3 hours reaction. Sulfonation reaction was terminated by precipitation process into ice water. Excess acid that contains sulfonated PEEK (sPEEK) sediment was flushed with water until neutral pH. Then, sPEEK polymer was dried in 60 °C for 48 hours.

Preparation of electrolyte membrane which is modified by inorganic additive was used phase-inversion method. The sPEEK was added by 1 %, 3 %, 5 % compositions of natural zeolite that we prepared before into n-methyl-2-pyrolidone (12,5 % of solution composition) until 24 hours. The bubbles that caused by agitation process was eliminated by allowed this solution in the room temperature condition for a night and washed by ultrasonic washer for 15 minutes. The polymer solution was casted on a glass plate. The 70-80 μm thin layer was formed and was dried in 60 °C for 48 hours to make permanent membrane.

2.4 sPEEK-zeolites Membrane Characterization for MFC System

Electolyte membrane characterizations for MFC system application in this research used proton conductivity (impedance spectroscopy) and water uptake measurement. Proton conductivity was measured using LCR-meter (HIOKI 3522-50 LCR HiTester). Electrolyte membrane must be fully hydration before measurement.
In the water uptake measurement, dry membrane was weighed before it has been soaked in deionization water for 24 hours. The wet membrane was weighed and was calculated by this equation.

\[
\text{% water uptake} = \frac{W_{\text{wt}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%
\] (1)

3 Results and Discussion

3.1 Active Natural Zeolites Characterization

Natural zeolites activation for this research was necessary to eliminate metal ions from natural zeolites. Elimination of their contaminants were done by acidification method. Acid that we used in this research is HCl.

<table>
<thead>
<tr>
<th>No</th>
<th>Zeolite</th>
<th>Treatment</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Natural Zeolites</td>
<td>HCl 37 % reflux 2 h, 37 °C</td>
<td>More greenness zeolites</td>
</tr>
<tr>
<td>2</td>
<td>Acid Zeolites</td>
<td>Aquadest flushing</td>
<td>Greenness White Neutral zeolites</td>
</tr>
<tr>
<td>4</td>
<td>Neutral Zeolites</td>
<td>NH\textsubscript{3} 33 % reflux 2 h, 37 °C</td>
<td>Alkali Zeolites</td>
</tr>
<tr>
<td>5</td>
<td>Alkali Zeolites</td>
<td>Aquadest flushing</td>
<td>Neutral Zeolites</td>
</tr>
<tr>
<td>6</td>
<td>Neutral Zeolites</td>
<td>Drying in 120 °C, 4 h</td>
<td>Active Zeolites</td>
</tr>
</tbody>
</table>

In this research, reflux process was done by using acid and alkali method in different aims. HCl reflux was done to eliminate anion impurities in the zeolite and NH\textsubscript{3} reflux was done to eliminate cation impurities.

Active natural zeolites were characterized in particle size parameter to know which is zeolites in the nano scale before modifying to the sPEEK polymer. It is important for improving active natural zeolites absorption ability in the modification with sPEEK membrane by making zeolite in the nano scale form.
By using PSA equipment, we know that active natural zeolite that we used in this research is approximately 437 nm in diameter particle. It described that particle we used is in the nano scale.

### 3.2. sPEEK-zeolites Membrane Characterization for MFC System

Zeolites have high selectivity to be used as cathion or proton adsorber. Proton selectivity property for zeolites depends on alumina and silica formation because ionic porous is developed according to their formation. This property will be helpful to modify sPEEK membrane as PEM.

<table>
<thead>
<tr>
<th>No</th>
<th>Membrane</th>
<th>Conductivity (S/cm)</th>
<th>Water Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>sPEEK</td>
<td>0.018</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>sPEEK + Zeolites 1 %</td>
<td>0.0125</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>sPEEK + Zeolites 3 %</td>
<td>0.028</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>sPEEK + Zeolites 5 %</td>
<td>0.02</td>
<td>20</td>
</tr>
</tbody>
</table>

In this research, we know that zeolites composition in the electrolyte membranes can increase their conductivity and water uptake properties. Proton exchange ability from zeolite will be stopped if they have equivalent chemical potential from inside zeolites and outside zeolites. Because of that, sPEEK + Zeolites 5 % has less conductivity than sPEEK + Zeolite 3 %.

Zeolites properties can increase water absorption in electrolyte membrane in this research. The more percentage of zeolites in electrolyte membrane the more water uptake percentage. The water uptake ability increased almost two times in
the presence of active natural zeolites in this research. Oxide frameworks in the zeolite can adsorb water and keep the water in the electrolyte membrane.

4 Conclusion

Active natural zeolites presence in sPEEK electrolyte membrane composition can increase conductivity and water uptake properties. But unfortunately, Proton exchange ability from zeolite will be stopped if they have equivalent chemical potential from inside zeolites and outside zeolites.

5 References


