Electrochemical Characterization of Direct Ethanol Fuel Cell (DEFC) with Bioethanol FeedContaining Acetic Acid as Impurity

Mitra Eviani*, Isdiriayani M. Nurdin*, Hary Devianto\(^{0}\)

Abstract

Direct ethanol fuel cell (DEFC) rises as an alternative future substitute to internal combustion engine. DEFC is able to utilize ethanol as the feed to directly generate electrical energy. Hence, unlike most of other types of fuel cell, fuel reforming to generate hydrogen is not necessary in DEFC system. Concerning future application of DEFC in Indonesia, utilization of bioethanol as DEFC feed is important to be studied, considering the abundant stock of biomass which is easily converted through fermentation process to bioethanol. However, in addition to low ethanol concentration, bioethanol production also produces by-products, consisting of organic compounds at significant amount. Acetic acid is one of the by-products resulted from hydrolysis and fermentation process. This study encompasses the effects of acetic acid concentration on DEFC performance. The effect of acetic acid concentration was studied at 100, 250, and 400 ppm of acetic acid in the feed containing 10% ethanol. The characterization was conducted electrochemically through potentiodynamic scan and electrochemical impedance spectroscopy (EIS). DEFC characteristics resulted from this research are expected to become the basis for DEFC future improvement.

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Introduction

The development of alternative power sources to substitute fossil fuel is an important issue at present. Fuel cell is an alternative source of energy that has recently attracted much attention due to its ability to generate energy by converting directly chemical energy in fuels into electrical energy with high energy conversion efficiency, without any noise and vibration, zero emissions, quick start-up, and scalable design [1, 2].

Common fuel cells, such as Proton Exchange Membrane Fuel Cell (PEMFC), utilize hydrogen as the fuel. Utilization of ethanol as fuel for such fuel cells requires ethanol to hydrogen converting system, e.g. ethanol-reforming system. Complexity of the integration between reformer system and fuel cell leads the rise of Direct Ethanol Fuel Cell (DEFC) as an alternative for PEMFC. The theoretical calculations show that DEFC exhibits better energy efficiency than integrated ethanol-reforming-PEMFC system [3-8].

Detail electrode and overall reactions of EFC are shown below.

Anode : \( \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \)

Cathode : \( \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \)

Overall : \( \text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \)

DEFC utilizes ethanol as the feed to directly generate electrical energy [3]. Ethanol as liquid fuel on DEFC has several advantages, e.g. ethanol can be easily handled, stored, transported, non-toxic, has low production costs, availability, high specific energy, and does not require high-pressurized storage system [3-8]. Therefore, research on DEFC has increased in recent years and ethanol shows more efficient compared to methanol and other higher alcohols as fuel on Direct Alcohol Fuel Cell (DAFC) [9].

Ethanol can be produced in large quantity through fermentation of biomass-containing component of starch, sugar, cellulose [10]. Indonesia’s stock of biomass available for being converted to bioethanol is claimed to reach 49,807 MW [11]. However, utilization of bioethanol as DEFC fuel potentially brings performance issue. There are some by-products from bioethanol production, such as organic impurities, water and organic acid, which are suspected to affect the performance of DEFC. Acetic acid is one of the by-products resulted from hydrolysis and fermentation process [12, 13]. This research emphasizes on the identification of the effects of acetic acid and determination of acceptable acetic acid concentration range, within which DEFC can operate without any substantial performance decay.

Methodology

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The experiments used a commercially-available DEFC stack. It was reported that ethanol concentration from fermentation ranged between 2 to 12 vole%[14]. In addition, it is suggested upon the DEFC user manual to limit the feed ethanol concentration within 5 to 15 vole-percent, above which the DEFC will not work properly due to the high ethanol crossover that will stop chemical reactions required for generate electricity [15]. Therefore, the ethanol concentrations were varied by 5, 10 and 15 vole%.

Ethanol concentration of 10 vole% was chosen for the experiments using acetic acid. Acetic acid concentrations were varied by 100, 250 and 400 ppm. Effects of acetic acid concentration were studied through electrochemical characterization, comprises of open circuit potential (OCP) measurement, potentiodynamic, chronopotentiometry, potentiodynamic, and electrochemical impedance spectroscopy (EIS). All electrochemical characterizations were performed using Gamry 3000 potentiostat. The schematic diagram for electrochemical characterization can be seen in Figure 1. Reversible hydrogen electrode (RHE) was utilized as reference electrode.

\[ j = nFv_l = nFk(T, E) c_l \]
\[ = nFk_0 e^{-\frac{\Delta G^0}{RT} + \frac{\Delta G_{ac}}{RT}} = j_0 e^{\frac{\Delta G_{ac}}{RT}} \] (1)

There are two activation terms in (1), which are exponential function of electrode potential, \( E \), and exponential function of chemical activation free energy, \( \Delta G_{ac} \). Chemical activation energy is predicted to be the main contributor to the potential drop in activation region as a consequence of the electrode structure and nature alteration. Increase in the acetic acid concentration to 250 ppm might impose side reactions which alters the electrode structure as well as membrane conductivity. On the other hand, further increase in the acetic acid concentration results in better performance.

**Results and Discussion**

**a. Performance Characteristics**

Figure 2. shows performance curves of DEFC in the presence of acetic acid at various concentrations. Ascending curves show the relation between potential – current and power while the descending ones depict the relation between potential versus current.

Potential drop, both in activation and linear region, is observed in Figure 2. as the acetic acid concentration is increased to 250 ppm. Vigier et al.[16] proposed the following equation:

![Schematic of the experiment](image1.png)

**Figure 1.** Schematic of the experiment

![Potentiodynamic characteristic for ethanol feed containing acetic acid 100, 250, and 400 ppm](image2.png)

**Figure 2.** Potentiodynamic characteristic for ethanol feed containing acetic acid 100, 250, and 400 ppm

![Potential versus time at current density 0.6 mA](image3.png)

**Figure 3.** Potential versus time at current density 0.6 mA

Figure 3. shows potential versus time when DEFC is set to maintain a specific current density of 0.6 mA/cm² for 900 seconds. The chosen current density is the current density of DEFC fed with ethanol and 100 ppm acetic acid where the power almost reaches maximum (Figure 2).

Curves in Figure 3. are resulted from chronopotentiometry, in which DEFC is actually forced to produce specific magnitude of current. Negative potentials indicate that instead of generating electricity, DEFC is given a charge by the potentiostat. This would suggest that DEFC fuelled with additional...
250 and 400 ppm were not able to maintain a specific reaction rate for the same duration that a DEFC fuelled with additional 100 ppm acetic acid was able to. After 4 seconds, DEFC with 250 and 400 ppm acetic acid stops operating. It would furthermore suggest that DEFC experiences significant durability drop in the presence of 250 and 400 ppm acetic acid.

b. Impedance Analysis

Figure 4. shows Nyquist plot of DEFC after being fitted with the equivalent circuit presented in Figure 5. The fitting parameters are presented in Table 1.

![Image](89x399 to 281x453)

**Figure 4.** Fitted Nyquist plot of DEFC with ethanol feed containing acetic acid 100, 250, and 400 ppm

![Image](281x453 to 89x399)

**Figure 5.** Equivalent circuit model

Trend of the Ohmic and charge transfer resistance confirms the findings presented in performance curve analysis. All resistances increase significantly when 250 ppm acetic acid was added to the feed. Meanwhile, introduction of higher concentration of acetic acid apparently imposes side reactions which alter the mass transfer behaviour of DEFC, indicated by formation of additional peak in the mass transfer region at 400 ppm acetic acid concentration. These results in the bias of charge and mass transfer resistances reading as the equivalent circuit model remain the same, particularly in the presence of 400 ppm acetic acid.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Acetic Acid Concentration (ppm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Ohmic</td>
<td>0.161</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>4.773</td>
</tr>
<tr>
<td>Mass transfer</td>
<td>2.785</td>
</tr>
</tbody>
</table>

**Table 1.** Fitting Parameters of DEFC

Conclusions

Addition of 250 and 400 ppm acetic acid in bioethanol fuel of DEFC was found to significantly alter Ohmic, charge transfer, and mass transfer resistances. It is finally concluded that acetic acid concentration in bioethanol shall not exceed 100 ppm to give acceptable DEFC performance.

References


