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The Effects of Electrolyte-Fuel Concentrations on Methanol-Based Alkaline Fuel Cell Through Non-Noble Metal Catalysts

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Abstract: Mostly, the research about Direct Methanol Alkaline Fuel Cell (DMAFC) concentrates on electrode catalyst and appropriate electrolytes to increase the efficiency. Mostly, a Pt-based electrocatalyst was used. In this research, Nickel foam and silver membrane as non-noble metal electrocatalysts were used in a square-shaped fuel cell stack of 15 x 15 cm in size. The flow of electrical charge is caused by the flow of hydroxide ions from nickel foam as an anode to the silver membrane as a cathode catalyst. Potassium hydroxide which plays an essential role in delivering hydroxide ions was used in this study. The electrolyte effect of potassium hydroxide was studied in different concentrations for the methanol oxidation reaction. Nickel foam and silver membrane were used for the methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR), respectively. 1 M, 3 M, 5 M concentration of potassium hydroxide and 0.5 M, 1 M, 2 M, 3 M, 4 M, 5 M of methanol as a fuel have been conducted. The highest maximum power density is 543.35 mW/cm^2 which is obtained at a current density of 2.331 mA/cm^2 using 5 M KOH and 0.5 M fuel. At equimolar concentration between fuel-electrolyte mixture give the higher current density.

Keywords:*Fuel Cells, Direct Methanol Alkaline Fuel Cells (DMAF), non-noble metal catalyst, nickel foam, silver membrane*

Introduction

Alternative sources of energy, the environment, and information of technology are the main focus of human civilization in the 21st, where humans try to live modern lives and stay in harmony with nature. One of the biggest challenges in the world today is finding, researching, and developing alternative energy sources that are effective and efficient, renewable, and do not pollute the environment. Fuel cells as substitutes for fossil fuels that are cheap, clean, and portable can answer that challenge. The fuel cell is an electrochemical device similar to a battery. However, fuel cells are designed to be continuously filled with reactants. It produces electricity by supplying hydrogen and oxygen from the outside [2].

Various types of fuel cells have been investigated in recent years. Among these types, Direct Alcohol Alkaline Fuel Cell (DMFC) can be used as a replacement for batteries in portable electronic equipment such as cell phones, laptops, alarm clocks, portable fans, etc [3-7]. Methanol is a liquid fuel that has many advantages over gaseous fuels such as hydrogen. Methanol is easier to handle, simple molecular structure, higher enthalpy, easy manufacture, and low operating temperature [8, 9].

The oxidation kinetics of the methanol is more fluent in alkaline electrolytes than acid electrolytes. This is very profitable and allows for using inexpensive metal catalysts that can facilitate the development of these fuel cells [10,11]. Most of the electro-catalytic reactions in fuel cells perform better in alkaline electrolytes. The electro-catalytic reactions are reduction of oxygen and oxidation of methanol. Fuel cells were first operated on alkaline media [12].

The direct use of liquid fuels as reactants to alkaline fuel cells has been studied for a long time. Some of which have been studied such as methanol [13–15], ethanol [13–15], and sodium borohydride [14–15].

The main components of a fuel cell are the electrode and electrolyte, where the electrode consists of a cathode and anode. The electrocatalytic reaction of methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) commonly using platinum as an anode electrode catalyst. The use of platinum with fuel cell commercialization is limited due to its high cost and poor performance against anodic reaction. The reaction of methanol on the surface of the platinum catalyst does not work well because the CO gas from the dehydrogenation of methanol blocks the surface of the catalyst. so the fuel cell power density decreases [4]. So the opportunity to use cheaper catalysts such as nickel, alumina, molybdate, and others is quite large. In addition, the oxidation reaction works well on alkaline electrolytes such as sodium hydroxide.

Various attempts have been made by many researchers for direct methanol fuel cell performance improvements over time. Manganese dioxide as a cathode catalyst was studied with different fuels for the oxygen reduction reaction in an alkaline electrolyte [16]. This work was continued in 2005, but still using platinum and Mangan dioxide as the electrocatalyst of anode and cathode. A special new electrolyte carrier plate design was investigated for alkaline fuel cells that use alcohol directly for their fuel [16]. This research also still used platinum as an electrode catalyst. They found that a new design electrolyte carrier can increase fuel cell performances. Platinum (2–5 $mg.cm^{-2}$) as anode and active carbon as a cathode was used in research by Kordesch et al [13]. In 2014 a glass carbon electrode was modified by ordering mesoporous Ni/Al_2O_3 to be used as anode catalyst [14]. The performance generated a low current density due to the use of sodium hydroxide as an ion-conducting electrolyte.

The flow of electrons in that alkaline fuel cell due to the flow of hydroxide ions. The flow of hydroxide ions is in the opposite direction to the electric current. Alkaline electrolytes as a medium for conducting hydroxide ions play an essential role. Because hydroxide ions are transported through the electrolyte along the direction of the electro-osmotic attraction against the flow of methanol. Thus, the resulting. CO_2 decreases with increasing KOH concentration. The carbonate salt deposition at the anode is caused by an increase in the KOH concentration in the system. So that the fuel oxidation reaction at the cathode decreases. The electrolyte concentration plays an important role in this fuel cell and must be optimized.

Although several kinds of research have been conducted on DMAFC, the electrolyte effect of potassium hydroxide to fuel concentration has never been reported. As a consequence, we conducted the electrolyte effect of potassium hydroxide to methanol as fuel through Ni-foam and membrane silver as a non-noble metal electrocatalyst.

Theoretical Background

Among the many types of fuel cells, Direct Methanol Alkaline Fuel Cell (DMAFC) is particularly interested in powering many portable devices. These fuel cells use methanol directly as fuel. These fuel cells can use both acidic and alkaline electrolytes. Methanol is a liquid at room temperature. Methanol is easy to handle and has high energy [13]. One molecule of methanol yields 6 electrons in stoichiometry in the electrochemical oxidation with the following reaction in figure 1.

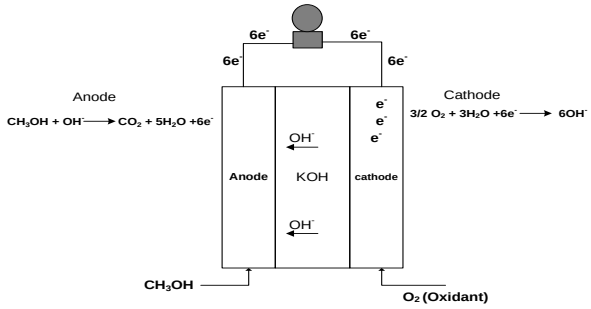

Figure 1.Operation mechanism of DMAFC

The working principle of Direct Methanol Alkaline Fuel Cell (DMAFC) is illustrated in figure 1. The porous silver metal membrane is a cathode electrode and nickel foam is an anode electrode. The electrolyte used is potassium hydroxide solution. The methanol solution is pumped towards the anode. The methanol molecules are oxidized and react with OH- to form five molecules of water, one molecule of carbon dioxide, and six electrons. Electrons flow to an external load to provide power. After that, the electron goes to the cathode via external load. The reduction reaction of oxygen occurs on the cathode side. At the cathode side, the OH- ions generated and diffuse past the electrolyte into the anode side for a continuous reaction. Electrocatalytic reactions of alcohol and oxygen in alkaline electrolytes are more current than in acid electrolytes.

Among many other metals, nickel is the most researched alternative Pt anode catalysts for the reaction of methanol in alkaline electrolytes [12]. Among the nickel types, nickel foam is produced

commercially on a large scale. On the other hand, nickel foam has a very porous structure and high surface oxidation area as well as excellent mechanical and electrochemical properties [15,16]. The $Ni(OH)_2$ layer will form on the surface area when nickel foam contact with alkaline electrolytes by the following reaction mechanism [16] :

$Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e^-$

$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$

$NiO(OH) + CH_3OH \rightarrow Ni(OH)_2 + product$

The NiOOH formed has an important role in the methanol oxidation reaction [14]. The porous silver membrane does not use carbon support, has a micro-pore size and high porosity. Thus increasing the active side of the catalyst.

Method

Set Up Method

The Fuel cell stack design is square-shaped 15 x 15 cm in size. The active area size of the electrode is 10 x 10 cm. The electrode and electrolyte chamber was made from a perspex sheet (acrylic material). Stainless steel was used as an endplate material.

Preparation of Material

Porous silver metal membrane (Purity 99,97%) with 1,2-micron thickness as a cathode electrode was purchased from Sterlitech Corporation. Nickel foam as anode electrode was purchased from Xiamen Tob Energy Technology (Purity 98%). A Copper sheet was used as a mechanical support for the silver membrane.

Concentrated Potassium Hydroxide solution was used in all experiments as the electrolyte. Analytical grade Methanol (E. Merck) was used as a liquid fuel. Oxygen as the oxidant was purchased from PT. Samator Gas Industri Palembang. Fresh demineralized water was used in this experiment

The electrode consists of anode and cathode. The cathode was coated with copper as mechanical support. Copper has excellent electronic conductivity, good carbon tolerance and has a low melting temperature so unstable and ductile at high temperature [20].

Different % weight of the mass of Potassium Hydroxide (KOH) pellet and Methanol (Analytical grade) was dissolved in the demineralized water. The solution of KOH and methanol was mixed for 1.5 hours at room temperature.

Results And Discussion

Figure 2 shows the methanol concentration-electric current relationship for three different KOH concentrations for methanol oxidation reaction respectively. The current density which is produced from methanol oxidation reaction was decreased in methanol increase respectively.

The decrease in density current with the increase in methanol is probably due to the lack of methanol availability at the anode. Increasing the concentration of methanol causes the availability of OH ions to decrease. So that the methanol oxidation reaction gets suffers. OH- ions are only slightly adsorbed on the outer layer of the catalyst. As a result, the current generated at the higher methanol concentration is reduced.

The higher the current, the more electrons will flow at a certain time. This means that the reaction is carried out rapidly on both the anode and cathode. This is in accordance with stoichiometry. At a KOH concentration rising from 1 M to 3 M does not show an increase in electric current. At equimolar fuel-electrolyte concentration show the highest current density. The highest maximum power density is 543.35 mW/cm^2 which is obtained at a current density of 2.331 mA/cm^2 using 5M KOH and 0.5M fuel.

In the use of equimolar concentrations of potassium hydroxide and methanol in the electrolyte, methanol and OHads species will chemically absorb and cover adjacent catalyst sites simultaneously (Verma and Basu, 2014). At 5M KOH concentration doesn't show the same result but increases the methanol concentration before. It's probably due to carbonate precipitation in the electrode surface.

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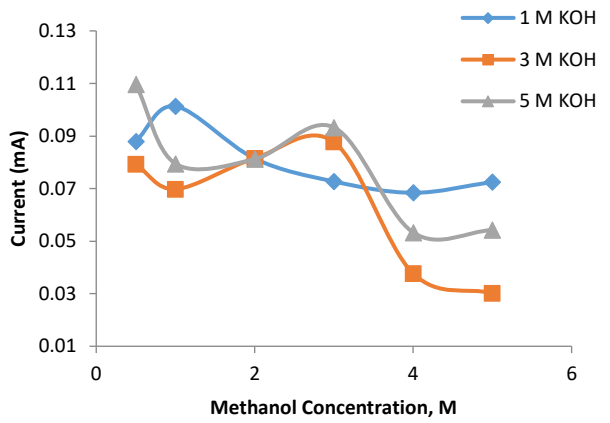

Figure 2.Methanol concentration-electric current curve with different Potassium Hydroxide concentration at 50 minutes operation.

Methanol crossover will occur when a higher methanol concentration contacts the anode and cathode. This can cause oxidation reactions at the cathode which is useless and inhibits the oxygen reduction reaction on the surface of the silver membrane.

Conclusions

This research was conducted to determine the effect of fuel-electrolyte concentration on alkaline fuel cell which using methanol as a fuel. The highest cell performance when used 5M KOH with 0,5M fuel. At equimolar concentration between fuel-electrolyte mixture give the higher current density. The highest maximum power density is 543.35 mW/cm^2 which is obtained at a current density of 2.331 mA/cm^2 using 5M KOH and 0.5M fuel.

The decrease in density current with the increase in methanol concentration is probably due to the lack of methanol availability at the anode. This poor performance of the system may be due to the crossing of the methanol to the silver membrane. In addition, the formation of carbonates due to the by-products of CO_2 gas can affect the performance of the electrocatalysts and alkaline electrolytes.

Conflicts of interest

"There are no conflicts to declare".

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