Faculty of Engineering

CROSS-LINKED CHITOSAN-SAGO COMPOSITE MEMBRANE FOR DIRECT METHANOL FUEL CELL APPLICATION

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Bachelor of Engineering with Honors
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HAMIZAN BIN PADIEL

This project is submitted to the
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The research and study of cross-linked Chitosan – Sago composite membrane used inside the direct methanol fuel cells is dedicated to the Faculty of Engineering, Universiti Malaysia Sarawak for better improvement in fuel cells mechanism, performance and research.

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ABSTRACT

Fuel cell is an electro chemical device that combines hydrogen and oxygen to utilize electricity and produce water and heat. Direct Methanol Fuel Cells (DMFCs) is one of the potential portable fuel cells mechanisms. The performance of the DMFC is depending on the Proton Exchange Membrane (PEM) technology. The research and studies in improving the performance of PEM used inside the DMFC has long developed. Few factors are still hindering the existing PEM. For example, Nafion 117 has high methanol crossover, expensive, unrecyclable and short lifespan. A good PEM should has high proton conductivity, high water uptake, less swelling, low methanol permeability and crossover, and contribute to a relatively high efficiency. The fabrications of new composite samples such as chitosan – sago composite membrane, were developed and compared towards the existing composite membrane, Nafion 117. Experiments were conducted to determine the water uptake of the chitosan – sago composite membrane, the methanol permeability, conductivity of the composite membrane and the efficiency of each composite sample. 10 composite membrane samples were prepared, 5 without cross-linked and another 5 vice versa. The reason for cross-linked is to improve the hydrophilic properties of the PEM itself. Major outcome of the results in this study should satisfy all the PEM properties as mentioned above. To conclude, one sample was then suggested as the most feasible composite membrane that can be applied on the mini DMFC application.

ABSTRAK

Sel basah merupakan sejenis sel elektro kimia yang menggabungkan hidrogen dan oksigen untuk menjana elektrik dan menghasilkan air dan haba. Sel basah berasaskan metanol adalah satu contoh sel basah yang mempunyai potensi untuk menjadi sel mudah alih. Prestasi sel basah adalah berasaskan metanol bergantung kepada teknologi membran yang digunakan. Kajian dalam memperbaiki membran yang digunakan di dalam sel basah telah lama dijalankan. Terdapat beberapa faktor yang mempengaruhi membran yang sedia ada. Sebagai contoh, Nafion 117 mempunyai kadar penyilangan methanol yang tinggi, mahal, tidak dapat di kitar semula dan jangka hayat penggunaan yang pendek. Membran yang baik mempunyai kadar pengaliran proton yang tinggi, kadar penyerapan air yang tinggi, kurang mengembang, rendah kadar ketertelapan dan penyilangan metanol dan mempunyai daya kecekapan yang tinggi. Penyediaan membran komposit baru seperti chitosan – sagu dijalankan dan dibandingkan dengan membran sedia ada Nafion 117. Experimen dijalankan untuk mengetahui kadar penyerapan air, kadar keterlapan metanol, kadar pengaliran proton dan kecekapan setiap sampel komposit yang disediakan. 10 sampel komposit disediakan, 5 tanpa rangkaian silang dan 5 sebaliknya. Tujuan rangkaian silang adalah untuk meningkatkan sifat hidrofili membran berkenaan. Hasil utama dalam experimen ini harus memuaskan sifat membran seperti di atas. Kesimpulannya, satu sampel telah dicadangkan untuk menjadi sampel yang paling sesuai digunakan dalam aplikasi sel basah metanol.

EXTENDED ABSTRACT

Direct Methanol Fuel Cells (DMFCs) is attractive fuel cells on several applications due to their low weight and volume and applied on small and medium size application. Proton Exchange Membrane (PEM) is a conductor which provides any migration of proton between the separations of the anode and cathode electrodes inside DMFC. Nafion 117 is widely use as PEM in DMFC but due to certain drawback such as high methanol crossover, expensive and high methanol permeability limits it usage. Chitosan is a natural product which is derived from an abundantly available natural biopolymer found in the exo-skeletons of crustacean. Chitosan is cheap, inert, hydrophilic, insoluble and less swollen. Sago is a food starch that prepared from carbohydrate material stored in the trunks of several palms and well known as almost a pure starch. When two particles is bond into one polymer chain to another and to ensure the stability of the composite membrane is called cross-linked. The preparation of chitosan are carried out using crab shells and consist of 4 steps; deprotenization (remove protein), demineralization (remove minerals), decoloration (remove colours) and deacetylation (remove acetyl group). The fabrications of chitosan - sago membrane are as follow. Chitosan flakes were dissolved completely into acetic acid solution. Then it is filtered and cast on glass plate to dry (24 hours) and then dried out inside an oven (24 hours, 60^{o}C). The dried membrane then neutralized into NaOH (5 min) and washed thoroughly. The process repeated by adding various proportion of sago starches (2.5%, 5.0%, 7.5% and 10.0% respectively) and then divided into two portions (5 without cross-linked, 5 cross-linked). Cross-linked process then carried out by immersing the samples into 0.5M H_2SO_4 for 24 hours. The electro catalyst ink is prepared by mixing small amount of carbon black, wet Pt, de-ionized water and then adding small amount of methanol and Nafion 117 solution and stirred for 10 minutes. After the catalyst ink had been prepared, it then coated onto the carbon paper and the attach samples were heat press (4 – 7 min, 130^{o}C). Results obtained from experiment conducted compares on both cross-linked and without cross-linked samples. For water uptake, without cross-linked samples shows better results compare with cross-linked samples. Without cross-linked samples absorb more water compare with cross-linked samples. High water uptake lead to high proton conductivity, which is good for the PEM applications. Without cross-linked samples produces a lower permeability compare with the cross-linked samples. The addition of sago helps to reduce methanol permeability and also leads to low methanol crossover. The proton conductivity test were carried out determine which samples contribute the highest conductivity. Without cross-linked samples gives higher conductivity than cross-linked samples due to its higher water uptake. The thermodynamics analysis was conducted to determine the efficiency of the DMFC using the chitosan –sago as PEM. Without cross-linked samples gives low efficiency with the higher methanol concentration. Cross-linked samples give much lower efficiency than without cross-linked samples might due to low water uptake and less absorbing. Overall, it concludes that without cross-linked samples perform better than cross-linked samples. The samples still cannot match Nafion 117 as it was used as comparison with all samples tested and still the best composite membrane used inside fuel cells application. Therefore without cross-linked samples (92.5% chitosan + 7.5% sago, 0.5M, 40^{o}C) is the feasible composite samples for the mini DMFC operation.

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^{o}C	-	Unit temperature (Degree celcius)
%	-	Percentage
Wt	-	Weight/Wet
mV	-	Mili-Volt
h	-	Time (Hour)
g	-	Weight (Gram)
H	-	Hydrogen
O	-	Oxygen
CH_3OH	-	Methanol
$C_7HF_{13}O_5S.C_2F_4$	-	Nafion
NaOH	-	Natrium Hydroxide
H_2SO_4	-	Sulfuric Acid
DMFC	-	Direct Methanol Fuel Cell
PEM	-	Proton Exchange Membrane
MEA	-	Membrane Electrode Assembly
σ	-	Conductivity
η	-	Efficiency
μ	-	Micro
M	-	Molarity

CHAPTER 1

INTRODUCTION

1.1 Fuel Cells

The highly demand of fossil fuel especially for the energy intensive in industries trigger severe energy crisis. Moreover the usage of this fossil fuel can emit a significant amount of carbon dioxide, carbon monoxide and other harmful gases, thus causing more pollution and aggregating the green house effects. [1]. Two major world crisis; the depletion of fossil fuel and the green house effect need to be diverse the solution in order to reserve and protected in the future.

One of the alternative ways to reduce dependency on fossil fuel usage and also the green house effect is by using fuel cells. Fuel cells are an electrochemical device that combines hydrogen and oxygen to utilizing electricity, from continuous chemical reaction and produce water and heat [2]. The supplied fuel will make the fuel cell to continuing to works and generate power. Since the conversion of the fuel to energy takes place via an electrochemical process rather than combustion process, the process is reported to be cleaner, less noise generated and have a relatively high efficiency. Fuel cells are also reported to have a relatively low carbon dioxide emission [2]. The utilization of fuel cells as an alternative source of energy has been reported to be the most promising ways for the energy sustainability for the present and the future.

1.2 Types of Fuel Cells

Fuel cells are classified based on the electrolyte and the electrochemical reaction. Each takes place in each type of fuel cells, what catalyst required the temperature range, types of electrolyte required and much more factors [3]. There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications. There are Alkaline Fuel Cells (AFC), Molten Carbonate Fuel Cells (MCFC), Phosphoric Acid Fuel Cells (PAFC), Solid Oxide Fuel Cells (SOFC) and Zinc Air Fuel Cells (ZAFC), Proton Exchange Membrane Fuel Cells (PEMFC) and Direct Methanol Fuel Cells (DMFC) [3].

1.2.1 Alkaline fuel cell (AFC)

AFCs can achieve power generating efficiencies of up to 70% and used widely on space technology such as NASA. They were used on spacecraft to provide both electricity and drinking water. Alkaline fuel cells use potassium hydroxide as the electrolyte and operate at 71.11°C. However, they are very susceptible to carbon contamination, so require pure hydrogen and oxygen [3, 4]. Chemical reaction occurs on each side of the electrode:

Anode Reaction: $2\ H_2 + 4\ OH^- \rightarrow 4\ H_2O + 4\ e^-$

Cathode Reaction: $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

Overall Net Reaction: $2\ H_2 + O_2 \rightarrow 2\ H_2O$

1.2.2 Molten Carbonate fuel cell (MCFC)

MCFCs use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert matrix, and operate at high temperatures (approximate 648.89ºC). MCFC require carbon dioxide, CO_2 and oxygen, O_2 to be delivered to the cathode. To date, MCFCs have been operated on hydrogen, H_2, carbon monoxide, CO, natural gas, propane, landfill gas, marine diesel, and simulated coal gasification products [3, 4]. Chemical reaction occurs on each side of the electrode:

Anode Reaction: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode Reaction: $3/2\ O_2 + 6\ H^+ + 6e^- \rightarrow 3\ H_2O$

Overall Cell Reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2\ H_2O$

1.2.3 Phosphoric Acid fuel cell (PAFC)

PAFCs are used commercially nowadays and have been installed in various places such as hospitals, nursing homes, hotels, office buildings, schools, utility power plants, landfills and waste water treatment plants. PAFCs use liquid phosphoric acid as the electrolyte and operate at about 232.22°C. One of the main advantages beside it cogeneration efficiency, it can use impure hydrogen as fuel. PAFCs can tolerate a CO concentration of about 1.5%, which broadens the choice of fuels they can use [3, 4]. Chemical reaction occurs on each side of the electrode:

Anode Reaction: $2 H_2 \rightarrow 4 H^+ + 4 e^-$

Cathode Reaction: $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$

Overall Cell Reaction: $2 H_2 + O_2 \rightarrow 2 H_2O$

1.2.4 Solid Oxide fuel cell (SOFC)

SOFCs use a hard, non-porous ceramic compound as the electrolyte, and operate at very high temperatures (around 982.22°C). SOFCs generate among the highest efficiency that is about 60% and can achieve the potential efficiency over 70% if combining a high-temperature fuel cell with a turbine into a hybrid fuel cell. SOFCs are suitable for stationary applications as well as for auxiliary power units (APUs) used in vehicles to power electronics [3, 4]. Chemical reaction occurs on each side of the electrode:

Anode Reaction: $2 H_2 + 2 O^{2-} \rightarrow 2 H_2O + 4 e^-$

Cathode Reaction: $O_2 + 4 e^- \rightarrow 2 O^{2-}$

Overall Cell Reaction: $2 H_2 + O_2 \rightarrow 2 H_2O$

1.2.5 Zinc Air fuel cell (ZAFC)

ZAFCs have a high operating temperature that enables internal reforming of hydrocarbons and generate hydrogen. Due to this advantage, the by-product heat can be used to generate high-pressure steam for industrial and commercial applications. The electrolyte for the ZAFC has some advantages; it cannot dry out, eliminating the need to carefully monitor and control anode and cathode moisture levels. Additionally, as a solid, no leakage of the electrolyte will occur. Due to the consumption of the zinc anode, this component requires replacing at intervals [3, 4]. Chemical reaction occurs on each side of the electrode:

Anode Reaction: $CH_4 + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

$Zn + OH^- \rightarrow ZnO + H + e^-$

Cathode Reaction: $O_2 + 2H^+ + 2e^- \rightarrow 2\ OH^-$

$O_2 + 4H^+ + 4e^- \rightarrow 2\ H_2O$

Overall Cell Reaction: $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$