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JURUSAN TEKNIK KIMIA FAKULTAS TEKNOLOGI INDUSTRI
UNIVERSITAS PEMBANGUNAN NASIONAL "VETERAN" YOGYAKARTA

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SEMINAR NASIONAL TEKNIK KIMIA "KEJUANGAN" 2006
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UNIVERSITAS PEMBANGUNAN NASIONAL "VETERAN" YOGYAKARTA

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PERFORMANCE IMPROVEMENT OF PROTON EXCHANGE MEMBRANE FUEL CELL USING SOL-GEL CASTING TECHNIQUE

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Abstract

The sol-gel casting technique has been used for the fabrication of membrane electrode assemblies (MEA) as a means for better distribution of metal catalyst, such as Pt, residing on the membrane surface. This in itself will make the catalyst used to be more efficient. The precursor contained Tetra Ethoxy Ortho Silicate (TEOS) as the silica source and Phosphotungstic acid (PWA) as the proton conductive material. The electrolyte membrane, Nafion 112 was impregnated with the precursor solution containing PWA and TEOS before its coated with the catalyst ink to produce the electrodes. The electrodes were fused with the gas diffusion layers (GDL) by hot press at 120°C and pressure 30 atm for 4 minutes to produce the membrane electrode assembly (MEA). Catalyst loading on the membrane surface varies from 0.38 until 0.475 mg/cm². Characterization of the membrane Electrode Assemblies (MEA) conducted by fuel cell test system. Comparison of sol-gel MEA to the commercial MEA at the same operation condition but lower catalyst loading in anode/cathode (0.471 mg/cm² for commercial MEA) and (0.43/0.43 mg/cm² for sol-gel MEA) show a better performance. The result of the experiment show sol-gel MEA produce more high current and voltage along test time during 12 hours, and show stability of current and voltage during 30 hours test time at ambient temperature. So that could be concluded that sol-gel process is applicable for membrane electrode assemblies, and have advantages improve performance of proton exchange membrane fuel cell (PEMFC).

Keyword: heteropolyacid, sol-gel, nafion, PEMFC

Introduction

At the moment Proton electrolyte membrane fuel cell (PEMFC) in process of development and not far from commercialization to be used as a power source in motor vehicle⁽¹⁾. The solid electrolyte used in the PEMFC is Nafion membrane (Du Pont) is relevant to use allows for greater than 1 Acm⁻² of current out put. Nafion membrane is relevant to use of low temperature below 100°C⁽²⁾. At high temperature and low humidity, membrane will shrink due to membrane dehydration cause the lack of the water molecule as proton carrier in the membrane, and at high current density or high humidity membrane will swell. Shrinking and swelling have an effect reduces proton conductivity of the membrane and degraded of the surface linking structure between membrane and catalyst surface. At temperature in the range of 50-90°C the catalyst is very sensitive to poison by CO. So that CO in fuel hydrogen must be limited below 10 ppm⁽¹²⁾. This matter cause the liquid fuel like gasoline and methanol cannot directly be used as a fuel. Many works have done to overcome the sensitivity of the CO catalyst by increase operating temperature of the fuel cell. But at high temperature above 100°C membrane is started to degrade and at 130°C structure of the membrane will change⁽¹⁶⁾.

The aim of this work is to modified Membrane Electrolyte Assemblies (MEA) focused on Nafion membrane 112 with introduce the hygroscopic material (Si) and secondary proton conductive material using heteropolyacid (Phosphotungstic acid) (PWA) to produce a good performance of MEA. The role of silica in the membrane, to increases the stability of the membranes at low and high relative humidity while at the same time increasing the resistance to fuel crossover by creating more resistance in the flow channels⁽⁴⁾.

The source of silicate is Tetra Ethoxy Ortho Silicate (TEOS). One of the problem arise on using silicate is has low conductivity. In order to increase conductivity of the layer, heteropolyacid (PWA) (H₃PW₁₂O₄₀nH₂O) is immobilized in the silicate matrix polymer, is used. Heteropolyacid in the composite membrane generally is introduced as second proton conducting species⁽¹⁹⁾. The aim is to constrict the pore in the polymer matrix create greater resistance to molecular migration of the unwanted species. In addition

heteropolyacid has been used successfully as promoter in the catalyst surface to increase stability to CO poisoning, and has the necessary characteristics to serve as a mediator for reductions⁽⁷⁻¹³⁾. We observed that Silicate and PWA can increase chemical and temperature stability, more retain water molecule and increase flexibility of the membrane so that the composite membrane could be operated at temperature above 80°C in low humidity without shrinkage⁽⁶⁾.

Material and Method

Composite membrane was prepared by⁽¹²⁾ by hot pressing the mixture of melt fabricable perfluorosulfonylfluoride copolymer resin (Nafion) with fine zeolite powder at 230°C.

In these investigations an embedded Si/PWA in the polymer matrix using sol-gel method to produce hybrid membrane was performed. The membrane was embedded through two steps, first heteropolyacid (PWA) was mixed with Tetra Ethoxy Ortho Silicate (TEOS) to form solution at room temperature. Ratio of SiO₂/PWA used in this experiment is 10:3 (w/w)⁽¹³⁾. TEOS in acid condition will to be hydrolyzed produce silanol (Si(OH)₄). Second step was entrapped both component in the polymer matrix during gelling reaction of the silicate that go on in situ during drying in vacuum oven at temperature 80°C 25 mmHg and during hot pressing at 30 atm and 120°C and PWA is entrapped in the silica matrix polymer.

Immobilizes PWA in a matrix porous have been conducted by⁽⁹⁾ Zeolite is used as matrix (super cage) to immobilize Phosphotungsticacid (PWA) by arranging ratio aluminum/silicate molecule of zeolite. In this process required cation for ion exchange and solvent to zeolite dealumination hence the process is expensive and is not simple.

To overcome this problem we choose the process to immobilized PWA in the silica matrix using sol-gel method. After PWA has been immobilized, than entrapped both material in the membrane matrix polymer using impregnation method to produce hybrid membrane (Nafion/Si/PWA). Membrane will use as solid electrolyte for the Proton Electrolyte Membrane Fuel Cell (PEMFC) at high temperature (above 80°C).

The whole procedure to modifies membrane electrode assemblies (MEA) using sol-gel method conducted by few step that are: a). Impregnation Nafion membrane using solution contain (TEOS, PWA, IPA, water). b). Drying impregnated membrane at room temperature. c). Casting the catalyst ink solution on both surface of the membrane to produce membrane-electrode. d). Drying membrane-electrode at room temperature. e). Drying membrane-electrode in vacuum oven at 25 mm Hg and 80°C during 30 minute produce dry membrane-electrode. f). Superimposed GDL on both side of the membrane-electrode and than hot press at 120°C and 30 atm during 4 minute. g). Test of the MEA using Arbin fuel test system to know activity of the catalyst. Scanning electron microscopy (SEM) to analyze the microstructure of the catalyst layer.

Gas diffusion layer (GDL) preparation

Diffusion layer forming composition was prepared as follows.

The first Vulcan (carbon black) a mount of 1850 mg with 56.37 g Iso Propyl Alcohol mixed using magnetic stirrer during 30 minute. The resultant mixture was added Polytetrafluoroethylene 666 mg (PTFE wt 60%) mixed using homogenizer for 30 minute. The diffusion layer forming composition was applied onto the carbon cloth and dried at vacuum oven at temperature of 120°C for 2 hour. The finally obtained diffusion layer exhibited carbon loading 4,17 mgcm⁻².

Catalyst layer preparation.

Catalyst layer forming composition was prepared as follow.

1826 mg 20 wt% Pt/C catalyst and 5.699 g deionized water (DI) were mixed and stir using mechanical stirrer for 3 minute. To mixture of the catalyst and DI water was added 2113 mg Nafion ionomer produced by (Du Pont) solution 10 wt%. Than mixed using magnetic stirrers for 5 minute. To the mixture added 3 gram of Iso Propyl Alcohol (IPA), mixed using magnetic stirrer for 3 minute. The finally obtained Pt loading on the surface is 0.38 mgcm⁻².

Membrane Electrode (ME) and preparation Membrane Electrode Assemblies (MEA).

Treatment of Nafion membrane.

Nafion 112 were treated to remove organic and metal impurities by refluxing in the 3% wt (H₂O₂) peroxide solution for 1 hour. Followed by refluxing in the boiling water for 1 hour. To remove trace organic and metal impurities membrane treated again in the 1 N sulfuric acid solution (H₂SO₄) for 1 hour. The membrane was then refluxed in the boiling water 3 times until pH of water was neutral.

Preparation solution as impregnant of the membrane.
0.45 gr. PWA crystal dissolve in the mixture of 1.04 gr Deionized water and 3.0027 gr Iso Propyl Alcohol (IPA). To the mixture was added 0.257 gr. Tetra Ethoxy Ortho Silicate (TEOS) and mixed using magnetic stir for 3 minute to produce homogeneous solution.

Impregnation of the membrane Nafion 112 in the solution.
Membrane is impregnated in the solution for 10 minute and than dried in room condition for 10-15 minute. Catalyst layer forming composition applied onto both surface of the impregnated membrane using brushing method to produce membrane-electrode (ME). After word ME is dried in room temperature for 10-15 minute and gas diffusion layer imposed on both surface of the membrane-electrode than drying is continuously in vacuum oven at temperature 80° and 25 mmHg for 30 minute.

Preparation Membrane Electrode Assemblies (MEA).
The membrane electrode assemblies (MEA) was prepared by hot pressing the GDE/ME/GDE sandwich (active area of electrode 50 cm^2). Hot pressed done at constant temperature at 120°C and at a pressure 30 atm for 4 minute produced membrane electrode assemblies (MEA). MEA was positioned in single cell test, which was then installed in the fuel cell test system (Arbin Fuel Cell Test System). The test station is equipped with the temperature, pressure, flow rate controller for fuel gas (H_2) and oxidant (air). Humidification system is used to make fuel and air in saturation condition.

Fuel cell test

Performance evaluation of the PEMFC use feed fuel is pure hydrogen and air as oxidant at atmospheric pressure and certain temperature. The flow rate of fuel equal 300 ml/minute while air flow rate is 600 ml/minute. Cell potential vs. current density measurements were then made under this condition.

Result and Discussion

Tungstophosphoricacid $\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4]$ (PWA) is an Heteropolyacid (HPA) with high conductivity, this will enhance membrane conductivity. The basic structural unit of PWA is the Keggin anion $(\text{PW}_{12}\text{O}_{40})^{3-}$ which consists of the central PO_4 tetrahedron surrounded by four W_3O_{13} sets linked together through oxygen atoms. These complex form channels, which can contain up to 29 water molecules in different hydrate phases. This variety leads to different protonic species and hydrogen bonds of different strength. The consequence is high proton conductivity at room temperature at around 0.18 S/cm/ Lower hydrates of PWA containing six water molecules are stable up to 180°C an important.

Immobilized of heteropolyacid in silicate matrix is very important due to PWA have big molecule size and very soluble in polar solvent. The main reason that HPAs are widely used is that their molecule sizes are extremely large. The structure of an anion of an HPA with Keggin structure is close to a sphere with a diameter of about 1 nm. If PWA could be formed like a "ship in a bottle" in a "cage, who's size is slightly larger than their anions, the HPA anions would not be able to diffuse out of the cage⁽¹⁰⁾.

Fuel Cell Test the System (FCTS)

Analyze the catalyst activity for various concentration have been conducted by using Fuel Cell Test System at certain temperature stoichiometry between hydrogen and oxidant. The result is compared to commercial MEA at the same operation condition. Current density Vs time curve for various catalyst loading depict by figure.1. While Figure 2 show the stability of the polarization curve for the catalyst loading 0.43 mg/cm^2 during 45 hour. Figure 3 show . Current Vs Time of the sol-gel MEA (Pt loading $0.38/0.38 \text{ mg/cm}^2$ at the anode and cathode)and Commercial MEA (Pt loading $0.38/1 \text{ mg/cm}^2$ at anode/cathode) at room temperature.

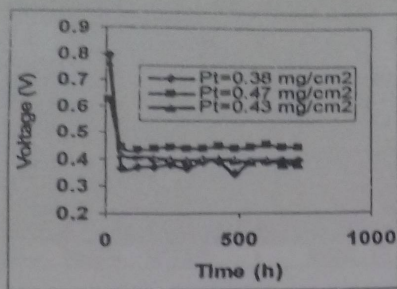


Fig.1. Current Vs Time of the MEA with various Pt loading, at room: temperature, stoichiometry H₂ : Air = 1:2.

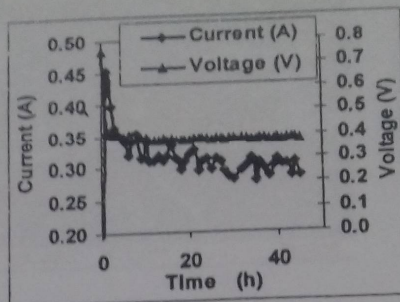


Fig.2. Polarization curve of the MEA with Pt loading 0.43 mg/cm² at room temperature, stoichiometry H₂ : Air = 1:2

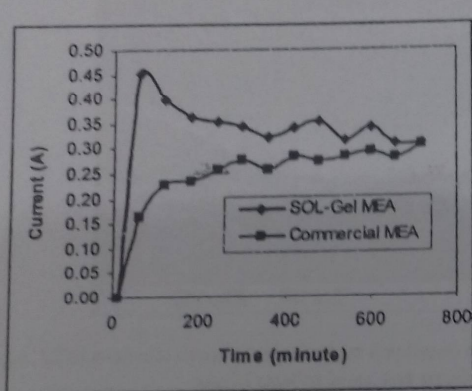


Fig. 3. Current Vs Time of the sol-gel MEA (Pt loading 0.38/0.38 mg/cm² at the anode and cathode) and Commercial MEA (Pt loading 0.38/1 mg/cm² at anode/cathode) at room temperature.

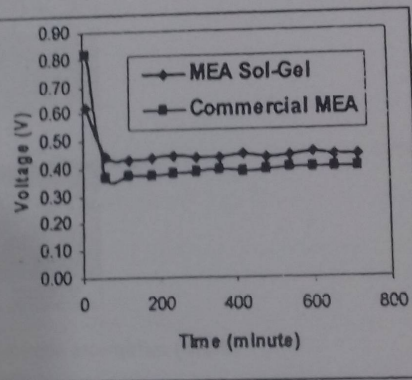


Fig. 4. Voltage Vs Time of the sol-gel MEA (Pt loading 0.38/0.38 mg/cm² at the anode and cathode) and Commercial MEA (Pt loading 0.38/1 mg/cm² at anode/cathode) at room temperature.

Scanning Electron Microscope (SEM)

Analyze the SEM needed to know the difference structure of catalyst layer using sol-gel casting and MEA conventional. Result of analysis expected difference of structure and pattern of spreading the catalyst particle over the electrolyte membrane. The result of SEM show for the MEA using sol-gel casting have Si/PWA thin layer (1 μ m) over two surface of the membrane. The role of the film is to manage water content in the membrane nafion 112 to overcome shrinking and swelling phenomena regarding better surface linking structure between catalyst and membrane so that the life time of the MEA increase.

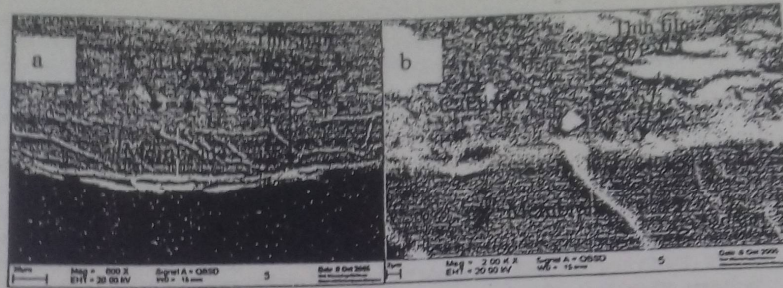


Fig.5. SEM analysis : Cross sectional of the membrane electrode assemblies (MEA) consist catalyst layer, Si/PWA film and membrane Nafion 112, a) Magnification 500 X and b) 2000X.

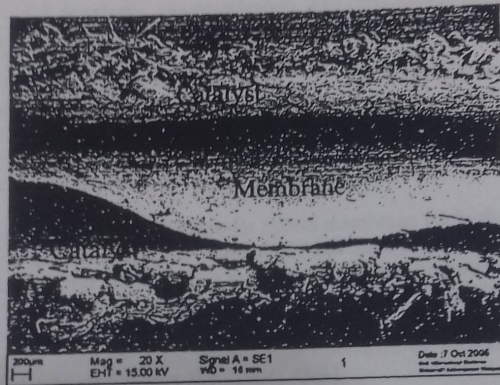


Fig.6. SEM analysis: Cross sectional of the membrane electrode assemblies (MEA) consist catalyst layer, and membrane

Conclusion

The sol-gel casting technique was employed to produce membrane electrode assemblies (MEA) of proton exchange membrane fuel cell (PEMFC), as a means for better distribution of metal catalyst, such as Pt, residing on the membrane surface. This in itself will make the catalyst used to be more efficient. To ensure the catalyst activity using this technique the experiment is conducted using various Pt loading on the surface of electrolyte membrane. The performance of the MEA has test using Fuel Cell Test System (FCTS) at the same operation condition, and the result shows as in fig.1. Current and voltage increase appropriate with increasing the catalyst loading from 0.38 until 0.47 mg/cm². The catalyst stability test during 45 hours and the performance stable at 0.4 V the current is 0.3 A as shows in fig.2., for the catalyst loading 0.43 mg/cm² at room temperature. In comparison with commercial MEA as in fig 3 and Fig.4. Shows the sol-gel MEA with lower loading produce a better voltage and current. The result of SEM analysis, show the characteristic of surface linking structure between catalyst and membrane layer. Fig.5 and fig.6 show clearly the difference structure between sol-gel MEA and MEA conventional . Sol-gel MEA show better surface linking between catalyst and membrane layer then conventional MEA. So that could to be concluded that sol-gel process is applicable for membrane electrode assemblies, and have advantages improve performance of proton exchange membrane fuel cell (PEMFC).

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