

# Electrochemical activities of hybrid nanocomposite membrane

Uma Thanganathan

Research Core Interdisciplinary Science, (RCIS), Okayama University, 3-1-1-Tsushima-Naka, Kita-Ku, Okayama, 700-8530, Japan

Tel.: +81 86 251 8706; fax: +81 86 251 8705; e-mail: ptuma2003@yahoo.co.in

## ABSTRACT

In this work, a hybrid composite membranes contain various concentration of phosphomolybdic acid (PMA) were successfully prepared and studied their performances of PEM fuel cells at low temperature by various operating time. The effect of heteropolyacid in composite membrane shows significant differences by electrochemical measurements and obtain the maximum power density of  $24 \text{ mW cm}^{-2}$  at  $40 \text{ }^\circ\text{C}$ , for hybrid electrolyte ( $\text{SiO}_2\text{-P}_2\text{O}_5\text{-PMA-GPTMS}$ ) contains the higher amount of PMA (15 mol %). The cell performances were increased considerably for all MEAs (membrane-electrode-assemblies) at similar operating condition. Over all observation, the cell life time is short. After short period, the cell did not showed any improvement of performances even cell stability was constant, the results were reported here.

**Keywords:** Pt/C electrode, PMA, Fuel cell, Hybrid membrane, Electrochemistry

## 1 INTRODUCTION

For fuel cell applications, the advantages of less expensive acid electrolytes having high proton conductivity and electrochemical activity in low temperature are desired [1-3]. Fuel cells are installed as a back-up supply for running medical equipment and experiments in hospitals. Thus it is evident that fuel cell technology shows a promise for reliability, flexibility and cleanness [4,5]. Fuel cells offer significantly higher chemical to electrical conversion efficiency, negligible or no or low exhaust pollutants, and multi-fuel capability, depending on the types of fuel cells [6]. Basically, the hydrogen-oxygen fuel cell consists of porous electrodes separated by an electrolyte. Hydrogen and oxygen diffuse through the anode and the cathode, respectively, and undergo reactions that create a potential difference across the cell. At the anode hydrogen molecules dissociate into atoms and then release electrons. The hydrogen ions flow to the cathode through the electrolyte, and the electrons flow through the external circuit. At the cathode oxygen molecules dissociate and accept electrons from the external circuit. The hydrogen and oxygen ions then combine to form water. A fuel cell consists of two electrodes sandwiched around an electrolyte. Oxygen passes over one electrode and hydrogen over the other, generating electricity, water and heat.

A fuel cell is essentially an energy converter, but it may be also considered as a chemical reactor depending on the

operating mode: (i) electric power generation (properly working as a FC); (ii) generation of electric power plus useful chemicals, (iii) generation of only useful chemicals as electrolytic cell, resulting from the consumption of external electric power. The fuel cell technology can be successfully employed in electronic applications: for example, when the generation rate of the corresponding product is desired to be increased, just as the hydrogen production (towards a hydrogen-based economy) [7]. Presently, there are several types of fuel cells, and among all of the different types of fuel cells, the PEM fuel cell is considered the most promising type. This is due to its desirable characteristics, such as quick start capability, low operating temperature, high power density and high energy efficiency [8, 9].

HPAs with the Keggin structure, and in particular the compounds  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  have received particular attention due to their acidic and redox properties, stability at elevated temperatures, commercial availability and relative ease of synthesis [10,11]. HPAs are known proton conductors, which may be exploited in the design of the membrane electrode assembly (MEA). Tatsumisago et al. [12] reported the proton conductivity value of silica containing PWA was about  $10^{-2}$  to  $10^{-1} \text{ S cm}^2$  at room temperature. Phototungstic acid (PWA) was successfully employed as an electrolyte in  $\text{H}_2/\text{O}_2$  fuel cells [13], as well as a surface promoter for CO-electro-oxidation [14]. The performance of a fuel cell depends on numerous factors. The electrolyte composition, the geometry of the fuel cell (particularly the surface area of the anode and cathode), the operating temperature, gas pressure and many other factors. In order that, in this work, we have concentrated study on cell performances were how much affecting by various composition of heteropoly-phosphosilicate hybrid composites at low temperature.

## 2 EXPERIMENTAL SECTION

The membranes were prepared by the sol-gel procedure, using silicophosphate ( $\text{SiO}_2\text{-P}_2\text{O}_5$ ) mixed with heteropolyacid (PMA) and 3-glycidylxypropyltrimethoxysilane GPTMS. The catalyst ink was prepared by mixing of Pt/C powder, Nafion with isopropyl alcohol. This mixture was well stirred for 1 day night in ultrasonic bath, after which the catalyst ink was sprayed smoothly on one side of the carbon sheet. It was dried at a low heat of  $60 \text{ }^\circ\text{C}$  for 1 h and then at  $100 \text{ }^\circ\text{C}$  for another 5 h, after which the other side was sprayed and dried under similar conditions. The membrane-electrode-

assembly (MEA) was prepared by hot pressing the Pt/C electrodes on both sides of electrolyte. The geometrical area of the electrodes was 1 cm<sup>2</sup>. The single cell was used to carry out fuel cell test (potentiodynamic and impedance measurements) at 40 °C with H<sub>2</sub>- based gas at the anode and O<sub>2</sub>- based gas at the cathode. Hydrogen and oxygen were supplied to the cathode and the anode sides at 20 and 50 mL min<sup>-1</sup>, respectively. At the heart of a proton exchange membrane fuel cell is a membrane electrode assembly (MEA), comprising of a proton conducting membrane sandwiched between two gas diffusion electrodes. The porous gas diffusion electrode structure consists of Pt/C electrocatalyst dispersed on high surface area carbon black, held together with a binding agent such as Nafion. The thickness of membrane-electrode-assembly was 1 mm.

### 3 RESULTS AND DISCUSSION

From the polarization curves in Figures 1, 2 and 3, the relation between power and current density values were noted for various compositions of SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-PMA-GPTMS hybrid ceramic composites (sample 1, 2 and 3) at 40 °C and relative humidity 100 % with various operating time. The maximum power density of 24 mW cm<sup>-2</sup> at 0.5 V for 7 h measurements, and the current density value of 114 mA cm<sup>-2</sup> for 78SiO<sub>2</sub>-5P<sub>2</sub>O<sub>5</sub>-15PMA-2GPTMS hybrid electrolyte [Figure 1], further there are no significant improvements during electrochemical measurements. The power density values of 15 and 16 mW cm<sup>-2</sup> and current density values of 58 and 73 mA cm<sup>-2</sup> were obtained for 83SiO<sub>2</sub>-5P<sub>2</sub>O<sub>5</sub>-10PMA-2GPTMS [Figure 2] and 88SiO<sub>2</sub>-5P<sub>2</sub>O<sub>5</sub>-5PMA-2GPTMS hybrid electrolytes [Figure 3] at above similar conditions. The hybrid membrane contains the heteropolyacid (PMA) concentration is 15 mol %, even to say the higher amount of PMA in the hybrid composite membrane shows the higher power density than other samples, but over all observation on all MEA shows the performances are not so high in the sense of expectation, even varied the concentration of PMA in the composite electrolyte. Therefore the duration of life time is short for cell in low temperature. One possible reason is due to the reaction between H<sub>2</sub> and electrolyte on the fuel cell operation condition. Because the electrolyte was reduced by H<sub>2</sub>, the interface contact between the electrode and electrolyte becomes poor which results in the high over potential at the electrode and the terminal voltage decrease. The destruction of electrolyte will also cause the decrease of conductivity of charge carriers.

The most common electrical test of a cell is a set of measurements that create the polarization curves [Figures 1, 2 and 3], which was simply the steady-state current vs. voltage curve of the cell. We have observed the curve shape was same as for all samples. In the activation region, the cell voltage drops quickly under even a small load current. This decrease begins when the load current exceeds the

normal forward/reverse reaction rate (exchange current) at the cathode. Parasitic corrosion reactions within the cell may alter the current where the cell voltage first begins to drop. After the initial drop, the cell voltage was continuously to decrease due to resistive losses in the ohmic region. In response to increasing load current in this region, the forward reaction at each electrode increases relative to the reverse reaction. It is the energy required to accomplish this chance that is indirectly responsible for the decrease in cell voltage. In this case, the part of the mass transport loss region was not appearing clearly in the polarization curve. Although not evident on the polarization curve, all three losses (active, ohmic, and mass transport) are present throughout its entire length. The ohmic losses appear small at low currents when compared to the activation losses in the first part of the curve. Likewise, the activation losses appear small when compared to the ohmic losses when the cell currents are larger (in the ohmic region). As cell voltage is reduced due to these losses, the electrical efficiency of the cell is also reduced. The MEA determines the total voltage, and the surface area of each cell determines the total current. Multiplying the voltage by the current will yield the total electrical power generated.

Electrochemical impedance spectroscopy (EIS) techniques can unravel different surface processes in the frequency domain, which makes it suitable for studying electrochemical processes on the catalyst surface. EIS principles and theories have been well explained by Macdonald [19], Bard et al., [20] and others. EIS has been widely used in other electrochemical research fields such as corrosion and lithium batteries. In recent years, EIS has also proved useful in fuel cell research [21-25]. AC impedance tools have the potential of isolating the various contribution to the fuel cell polarization curve [26], and methods have been demonstrated to determine pure ohmic (sum of electronic and membrane protonic) resistance as well as the protonic resistance within the cathode catalyst layer [27].

Figures 4, 5 and 6 shows a typical impedance spectrum of the single cell measured at 0.5 V using a two electrode configurations. The intercept with the real axis at the highest frequency represents the resistance of the electrolyte and the resistance of electrical connection wires. A complete electrochemical characterization using impedance spectroscopy and steady state performance was done to evaluate this technology. The total ohmic cell resistance values were noted for each samples [Figures 4-6] by various operating time and observed the total ohmic cell resistance values are high for 1 h measurement, and then it was decreased for another hour continuously decreased, but the charge transfer resistance values are still high and cell life time is not so long. The total ohmic resistance value of 78SiO<sub>2</sub>-5P<sub>2</sub>O<sub>5</sub>-15PMA-2GPTMS hybrid membrane display the 4.35 ohms [Figure 4], and obtained high power density.

### 4 SUMMARY

For the PEMFC using hybrid membrane contains various concentration of PMA, the maximum power and current density was  $24 \text{ mW cm}^{-2}$  and  $113 \text{ mA cm}^{-2}$  at  $40^\circ\text{C}$  with relative humidity 100 % for higher content of PMA in the hybrid composite membrane. But the stability for long time performance is still poor, because of the reaction between hydrogen and electrolyte at low temperature. Further to be achieving the cell performances by should be higher temperature using hybrid electrolytes.

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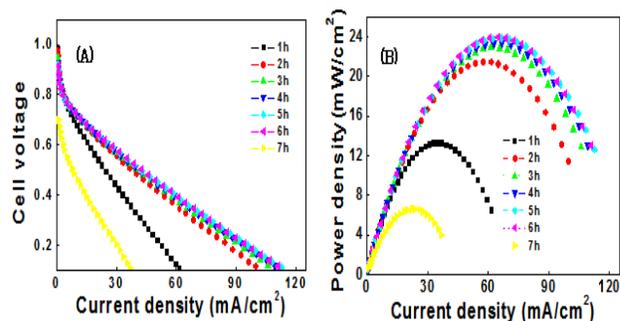


Figure 1: Current-voltage (A) and current-power (B) characteristics of MEA fabricated with  $78\text{SiO}_2\text{-}5\text{P}_2\text{O}_5\text{-}15\text{PMA-}2\text{GPTMS}$  hybrid composite electrolytes by various operating time.

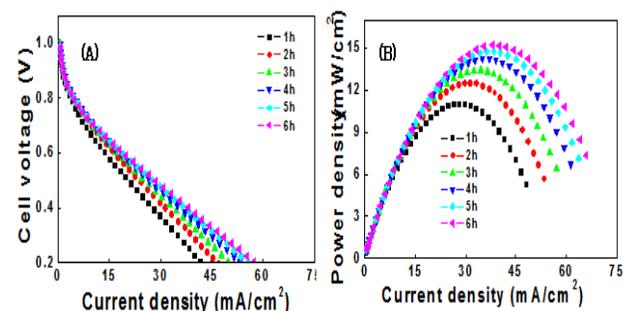


Figure 2: Current-voltage (A) and current-power (B) characteristics of MEA fabricated with  $83\text{SiO}_2\text{-}5\text{P}_2\text{O}_5\text{-}10\text{PMA-}2\text{GPTMS}$  hybrid composite electrolytes by various operating time.

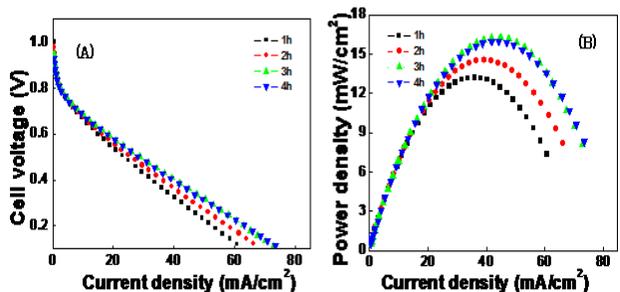


Figure 3: Current-voltage (A) and current-power (B) characteristics of MEA fabricated with 88SiO<sub>2</sub>-5P<sub>2</sub>O<sub>5</sub>-5PMA-2GPTMS hybrid composite electrolytes by various operating time.

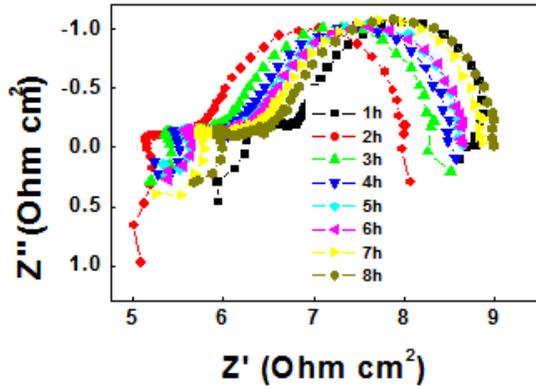


Figure 4: Typical impedance spectra of the single cell: Ac impedance curves measured at 40 °C for 78SiO<sub>2</sub>-5P<sub>2</sub>O<sub>5</sub>-15PMA-2GPTMS hybrid composite electrolytes by various operating time.

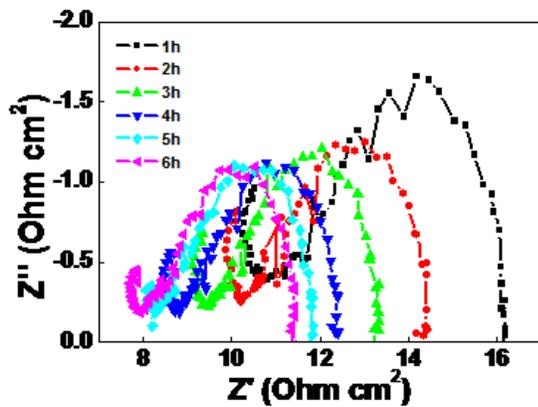


Figure 5: Typical impedance spectra of the single cell: Ac impedance curves measured at 40 °C for 83SiO<sub>2</sub>-5P<sub>2</sub>O<sub>5</sub>-10PMA-2GPTMS hybrid composite electrolytes by various operating time.

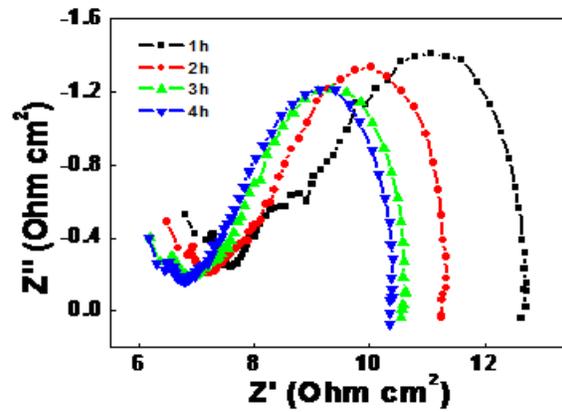


Figure 6: Typical impedance spectra of the single cell: Ac impedance curves measured at 40 °C for 88SiO<sub>2</sub>-5P<sub>2</sub>O<sub>5</sub>-5PMA-2GPTMS hybrid composite electrolytes by various operating time.