

Direct glycerol alkaline fuel cell fabricated using Au/C and microporous membrane

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ABSTRACT

The Au/C catalyst prepared by using the PVA techniques was used as an anode catalyst for the direct glycerol alkaline fuel cell. The Au/C catalyst contains 20%wt of well dispersed Au nanoparticles on Vulcan XC-72R carbon with an average size of 3.7nm (Yongprapat 2012). The microporous polypropylene sheet Celgard 3401 was used as a membrane. The single cell provided a maximum power density of 18.65 mW cm⁻² which was higher than the single cell with a commercial PtRu/C anode at 14.84 mW cm⁻². The constant potential tested for 30 minutes indicates a lower current decaying for Au/C fuel cell. The better performance was due to the lower activation loss of Au/C as implied by impedance results. The humidification condition at the cathode had an unnoticeable effect on cell performance. The V-I curves of the fuel cells with humidified oxygen at 70°C and unhumidified oxygen at the cathode were almost the same. This indicates adequate transfer of water and hydroxide ions from anode to cathode side of the cell.

1. Introduction

The electrode reactions of a fuel cell in an alkaline were operated different from that in an acid environment. This makes a number of catalyst materials to be chosen from for both anode and cathode. With this advantage, a more reaction selective catalyst can help alleviate a crossover problem. The required function of the membrane is only to provide the electrical resistance between both electrodes. The use of porous membranes without transport selectivity is possible. They are relatively cheap and with a variety types possible.

Lately, Au-based catalysts receive much attention for alcohol electrooxidation in alkaline type fuel cell (Padayachee 2013, Yongprapat 2012, Xin 2012, Zhang 2012). It shows higher catalytic activity than Pt-based catalysts for electrooxidation of polyhydric alcohols such as ethylene glycol and glycerol in alkaline solution (Yongprapat 2012). In

this study, we report the performance of the direct glycerol alkaline fuel cell based on microporous polymer fuel cell using Au/C. The Au/C was synthesized by using PVA protection method. The performance of fuel cell using Au/C anode catalyst under various single cell conditions was observed in comparison with PtRu/C.

2. Methodology

2.1 Catalyst preparations

The detail on the preparation of the Au/C catalyst used in this study was described in our previous work (Yongprapat 2012). In brief, the Au sol was prepared by using PVA protection method. The Au precursor was reduced to form Au nanoparticles by NaBH_4 in the presence of PVA. After that, the Au sol was immobilized onto Vulcan XC-72R supports to obtain the 20 %wt Au/C catalysts

2.2 Catalyst layers and MEA preparations

The catalyst layer ink was prepared by mixing a required amount of catalyst with isopropanol and a 5 wt% Nafion solution (Electrochem Inc.) in an ultrasonic bath for at least 30 min. The metal loading of the anode catalysts, Au/C or PtRu/C (E-tek), was at 1 mg cm^{-2} . The cathode catalyst for all cells was Pt/C (E-tek) loaded at 2 mg cm^{-2} . The well-mixed catalyst ink was painting onto a 5 cm^2 commercial gas diffusion layer (GDL) (ELAT, E-tek). The painted electrode was dried in vacuum over at $70 \text{ }^\circ\text{C}$ for 30 min.

The Celgard 3401 (Celgard Inc.) membrane was soaked in 2 M KOH solution for 30 min. After dried in ambient air, the MEAs were fabricated by sandwiching the membrane with the anode and cathode gas diffusion electrode (GDE). The MEA was clamped both sides by bipolar plates and current collector end-plates (Electrochem Inc.). The single cell was tightened at torque of 30 in lb.

2.3 Operation of single cell in fuel cell apparatus

A single cell with approximately 5 cm^2 was used in this study. The anode was fed by a fuel mixture of glycerol in KOH solution at 1 ml min^{-1} . Pure oxygen with or without humidification was fed at the cathode at a rate of 46 ml min^{-1} . The single cell was activated by the fuel and O_2 for 30 min prior to the performance evaluation. The polarization curves were measured via N3306A electronic load (Agilent). The data was recorded at the current density higher than 10 mA cm^{-2} due to the limitation of the electronic load. The electrochemical impedance spectra were measured using PGSTAT 302N (Autolab) with NOVA program. Impedance spectra were measured at a constant current density of 50 mA cm^{-2} in a frequency range between 5 kHz and 0.05 Hz with 10 points per decade, at the amplitude lower than 10 % of current discharged.

3 Results and discussion

3.1 Fuel cell performance

The Au/C catalyst used was well-dispersed Au nanoparticles on Vulcan XC-72R with average size of 3.81 nm (Yongprapat 2012). Fig. 1 and Fig. 2 show the polarization and power density curves of the single cell contained the prepared Au/C

catalyst at different cell temperatures and humidification conditions. The performance of the cell substantially depended on the cell temperature. The current density at 0.4 V was greatly improved from 18.1 mA cm⁻² at 40 °C to 27.2 and 38.9 mA cm⁻² at 60 and 70 °C, respectively. The highest power density at 70 °C was 15.82 mW cm⁻² at 0.35V. The current density increasing rate higher than one fold can be expected since the electrooxidation of glycerol on Au-based catalysts involves the C-C bond breaking. The main electrooxidation products were the C₁ and C₂ molecules (Yongprapat 2012).

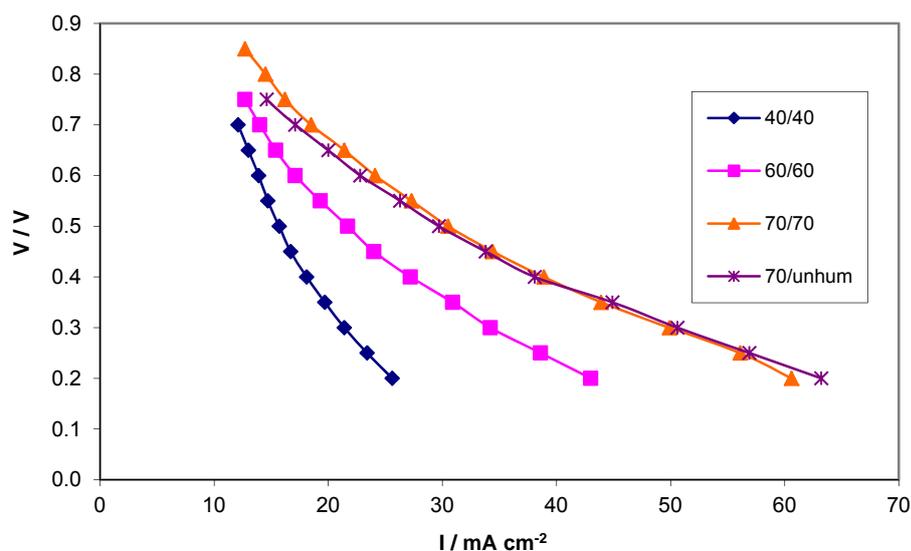


Figure 1 Polarization curves of the single cell using Au/C as an anode catalyst. Fuel feed is a solution of 1 M glycerol and 2 M KOH. The name of each curve defines the cell temperature and humidified temperature; 40/40 means cell temperature is 40°C and humidified temperature at 40°C.

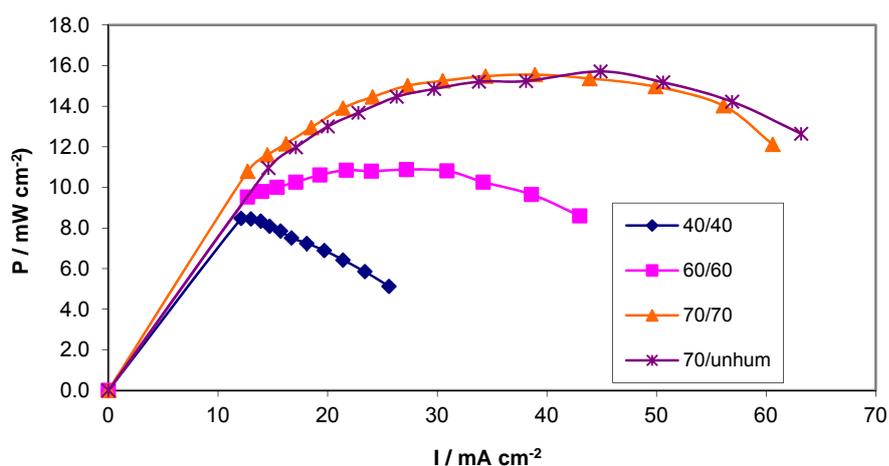


Figure 2 Power density curves of the single cell using Au/C as an anode catalyst. Fuel feed is a solution of 1 M glycerol and 2 M KOH.

The humidification condition at the cathode showed no effect on the cell performance. The polarization curve of cell operates at 70 °C humidification was overlay on that of the cell without humidification. Unlike in acid environment, water was one of the reactant of the cathode reaction of alkaline type fuel cells:



Inadequate amount of water should limit the cell performance. Without cathode humidification, water must be transported from the anode. Thus, transportation of the water was one of the crucial properties of the membrane.

The overlay of polarization curves here indicated a sufficient water transport through the pore of the membrane. For a reference, the Celgard 3401 used in this study has 41% porosity with 25 μm thickness. The thin and high porosity of this membrane ensure the water crossover.

Fig. 3 shows a short-term current density decaying at a constant voltage of 0.4 V and various cell operating conditions. The current was high in the first minute after current interrupt. The current becomes steady with a small decay after 1 minute. The current density obtained after the first minute, as shown in Table 1, was close to those from the polarization curves. The current density was much improved at higher cell temperature.

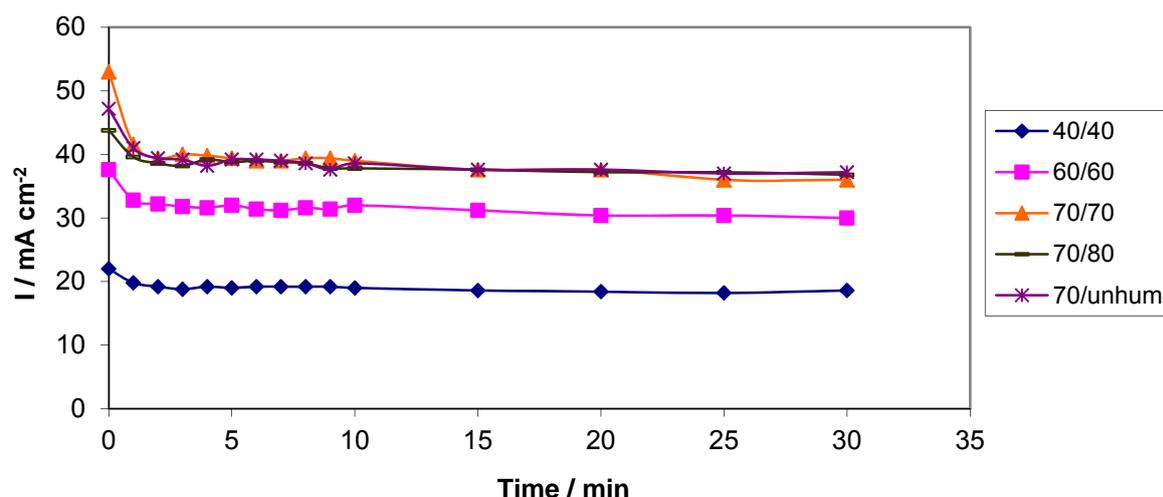


Figure 3 The current density decay of the single cell in Figure 1 at 0.4 V.

Table 1 Current density in mA cm⁻² unit and the decay rate from the 1st minute and 30th minute of the single cell in Figure 1 at 0.4 V.

$T_{\text{cell}}/T_{\text{hum}}$ (°C)	I at 1 st min	I at 30 th min	Current decay (%)
40/40	19.8	18.6	6.06
60/60	32.8	30.0	8.54
70/70	41.6	36.0	13.46
70/unhum	41.0	37.2	9.27

As time passes, the current density was slowly declined with a small variation. The current density was quite constant at low temperature but dropped faster at an elevated

temperature. The current density decline at 40 °C was at 6.06 % but became 13.46 % at 70 °C. The high decaying rate may result from several causes. First, the faster reaction rate at higher temperatures resulted in higher turnover frequency of glycerol electrooxidation, as a consequence, produced higher amount of poisonous products. Second, the glycerol electrooxidation was a complex reaction involves a number of steps via parallel pathways (Yongprapat 2012). The change in temperature can cause a change in a product distribution.

The humidify condition was still not a problem in the study condition. Long period of unhumidification did not affect the cell performance. The current decay in unhumidified condition was lower than that of the humidification one. Normally, an absence of humidity at the cathode should promote the transport of the anode to the cathode. Despite a non-selective porous membrane, along with the water and hydroxide, the glycerol was also transferred. The lower current decay rate may point out a low seriousness of the glycerol crossover from anode to cathode in this study setup. However, this was a subject for further study.

3.2 Comparison between Au/C and PtRu catalyst

This section compares the performance of the single cell using Au/C and PtRu/C as an anode catalyst. All the single cells were constructed in the same way as previously described. The cell performance was compared at 70 °C of cell temperature and humidification temperature. The glycerol concentration remains at 1 M but the KOH concentration was varied at 2 M and 4 M.

Fig. 4 and Fig. 5 show the polarization curves and power density curves of the single cell using Au/C and PtRu/C catalyst at both concentrations of KOH. The results indicated a superior activity of the Au/C catalyst for glycerol electrooxidation. Performance of the single cell with Au/C was higher than that using PtRu/C in the same condition. The maximum current densities of the single cell with PtRu/C were 33.2 and 37.1 mA cm⁻² at 2 and 4 M KOH, respectively, while that of the Au/C single cell was at 38.9 and 46.4 mA cm⁻² for the same condition. This reflect from the fact that the Au-based catalyst was more active for glycerol electrooxidation in alkaline than PtRu/C (Yongprapat 2012).

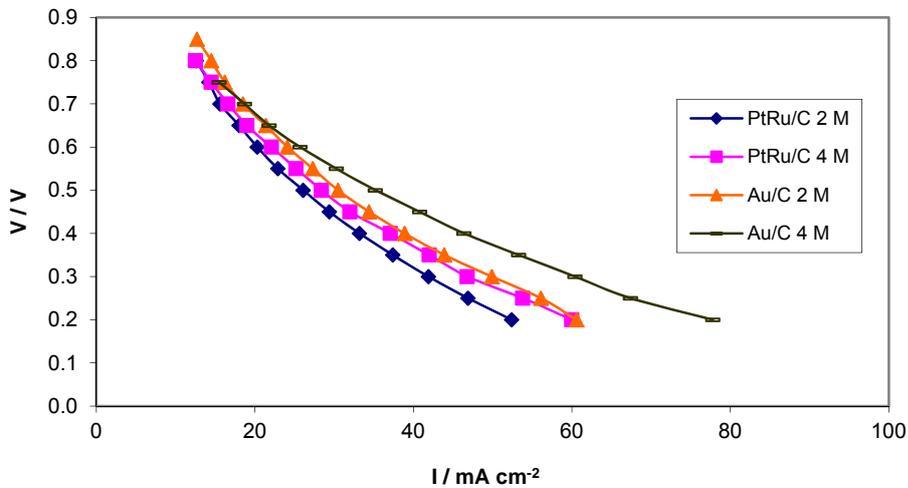


Figure 4 Polarization curves of the single cell using Au/C and PtRu/C as an anode catalyst using 1 M glycerol with 2 or 4 M KOH mix fuel at 70 °C.

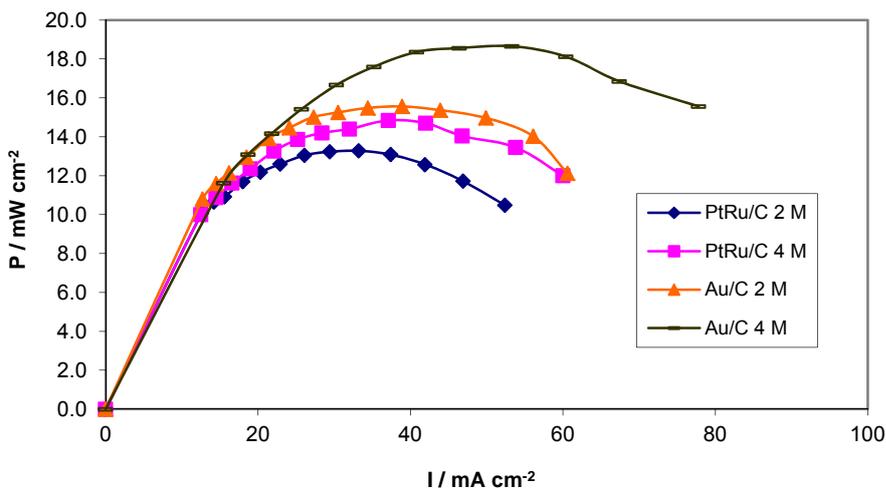


Figure 5 Power density curves of the single cell in Fig. 4.

Increasing KOH concentration improves the activity of both single cells. The increasing rate was much higher for Au/C than for PtRu/C at 19 % and 11 %, respectively. The addition of hydroxide solution provides different benefits to Au- and Pt-based catalysts. For Au-based catalyst, the rate determining step of glycerol electrooxidation was the adsorption of alcohol on Au surface. This process was either induced by the pre-adsorbed hydroxide on Au surface (Betowska-brzezinska 1997) or the adsorption of deprotonated alcohol (Kwon 2011). Increasing KOH concentration promoted both mechanisms and the overall reaction rate. For Pt-based catalyst, the rate determining step was the removal of the poisonous species from the catalyst

surface. Hydroxyl on Pt surface was used to remove the poisonous species via a bifunctional mechanism (Watanabe 2003).

Fig. 6 shows the current density decay curves at 0.4 V for single cell in Fig. 4. The current density trend was similar to that of the polarization curves. The single cell with Au/C yields the highest current density at 50.6 mA cm^{-2} , as shown in Table 2. The decay of all the cells was higher than 10 %. The decay in 2 M KOH of PtRu/C was slightly lower than that of Au/C. The decay of current density was higher with increasing KOH concentration. This was a result from a better activity of the catalyst. As KOH concentration was increased, the deactivation of the single cell with PtRu/C was almost one fold higher, while that of Au/C slightly increased. As a result, the single cell using Au/C became more stable.

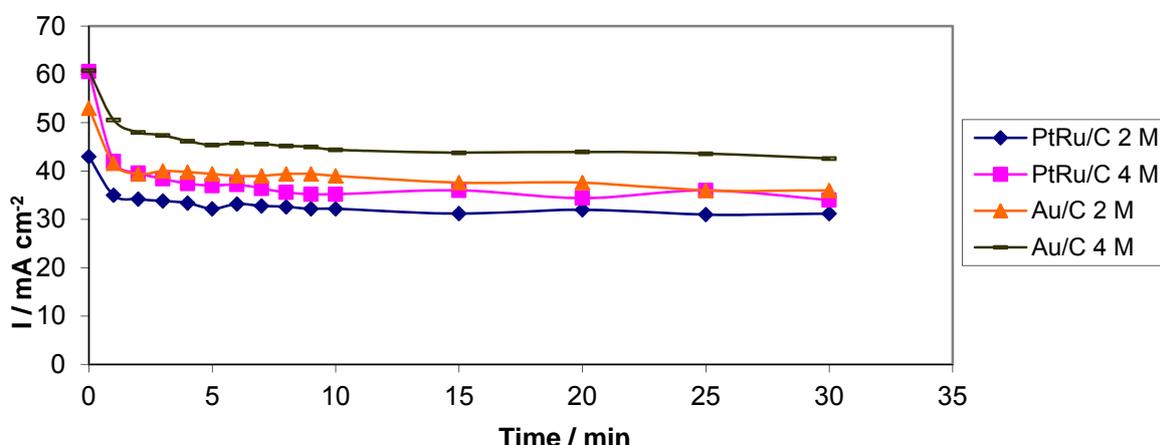


Figure 6 The current density decay of the single cell in Figure 4 at 0.4 V.

Table 2 Current density in mA cm^{-2} unit and the decay rate from the 1st minute and 30th minute of the single cell in Figure 6 at 0.4 V.

Catalyst	KOH (M)	I at 1 st min	I at 30 th min	Current decay (%)
PtRu/C	2	35.0	31.2	10.86
	4	42.0	34.0	19.05
AuL/C	2	41.6	36.0	13.46
	4	50.6	42.6	15.81

3.3 Impedance measurement

The impedance measurement was used to measure the activation loss of the single cell. The impedance spectra of single cell using Au/C and PtRu/C at a constant current of 50 mA are shown in Fig. 7. The activation loss can be observed from the intersection of the higher frequency arc on the real axis. The intersection of the single cell with Au/C was around 2 Ohm. For the single cell with PtRu/C, the intersection should be by far higher than 2 Ohm. This indicates a much lower activation loss of the Au/C catalyst over PtRu/C.

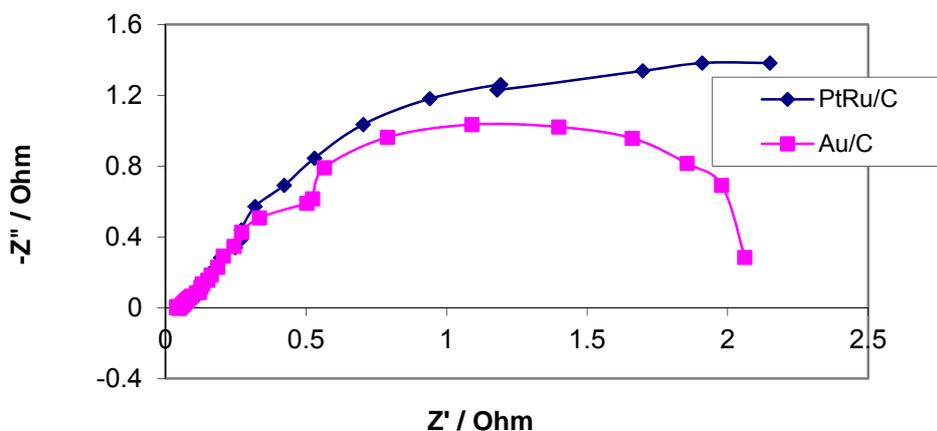


Figure 7 the impedance spectra of the single cell using Au/C and PtRu/C at a constant current density of 50 mA. Cell was operated at 70 °C, anode feed: 1 ml min⁻¹ of 1 M glycerol and 2 M KOH, cathode feed: O₂ at 46 ml min⁻¹.

4. Conclusions

The performance of Au/C prepared by PVA protection method for direct glycerol alkaline fuel cells using microporous polymeric membrane was evaluated in comparison with PtRu/C. The performance of both single cells greatly depended on the cell temperature. The current density was increased around 1 fold when the cell temperature was increased from 40 to 70 °C. However, the cell performance did not depend on the humidification condition at the cathode. This pointed out the sufficient water transferred from the anode to the cathode.

The single cell using Au/C showed better performance than that of PtRu/C in every condition. The current densities at 0.4 V for the single cell operated at 70 °C using Au/C and PtRu/C were 38.9 and 33.2 mA cm⁻² with the maximum power density at 15.56 and 13.28 mW cm⁻², respectively. The impedance spectra indicated the lower activation loss of Au/C over PtRu/C. The performance was improved at higher KOH concentration. The current density of the single cell using Au/C was increased to 46.4 mA cm⁻² with the maximum power density of 18.56 mW cm⁻².

The results show that the porous membrane was capable for the alkaline direct alcohol fuel cell. However, the cathode catalyst in this study was active for glycerol electrooxidation. Thus, it was suffer from the glycerol crossover. The type of catalyst at the cathode and the fuel cell structure was the subject for our study.

Acknowledgements

This work was financially supported by the Joint Graduate School of Energy and Environment (JGSEE) and the National Nanotechnology Center of Thailand (NANOTEC). The first author would like to thank the Royal Golden Jubilee (RGJ) program of the Thailand Research Fund (TRF) and JGSEE for the jointed academic scholarship.

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