Influence of thermal treatment on PtAu/C catalyst for glycerol electrooxidation in alkaline media

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Abstract:
The Au-based catalysts were prepared by using polyvinyl alcohol protected method. The physical and electrochemical properties of the as-prepared catalysts were measured. The catalytic activity and stability of the PtAu/C catalysts toward glycerol electrooxidation were measured using cyclic voltammetric and chronoamperometric methods. To promote the alloy formation between Au and Pt, heat treatment of the catalyst was performed with PtAu/C in a temperature range of 300-700°C at a heating rate of 10°C/min of under nitrogen atmosphere. The alloying degree of the heat-treated catalyst increased with increasing heat treatment temperature. Consequently, the significant enhancement of the onset potential of glycerol oxidation was achieved for the catalyst treated at 700°C. Moreover, The H-300 PtAu/C catalyst exhibited the lowest decay rate. However, the heat treatment also promoted sintering phenomenon of the metal particles leading to the decrease of the maximum current density. Therefore, the untreated PtAu/C showed higher performance than the heat-treated one.

Keywords: *glycerol electrooxidation; thermal treatment; polyvinyl alcohol (PVA) protection; PtAu/C; AAEMFC*

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1. Introduction

Nowadays, Glycerol is the promising alternative fuels for fuel cell devices because of its cost-effectiveness, plentifulness, and safety but glycerol oxidation reaction is quite slow. Although many studies have shown that Au/C catalyst exhibits high activity in glycerol oxidation. The gold-based catalyst can be further improved by adding a second metal. For bimetallic catalyst, heat treatment process is suggested as a necessary step to increase degree of alloying of the synthesized catalysts. However, heat treatment process has a significant impact on structural changes, such as particle size, and surface morphology. Therefore, the effect of heat treatment temperature on the performance of a PtAu/C catalyst was explored.

2. Methodology

Au/C catalyst was prepared by the PVA protection method (Yongprapat et al., 2012), using $HAuCl_4 \cdot 3H_2O$ as a metal precursor. The Au precursor was mixed with PVA solution and then 0.1 M $NaBH_4$ solution was added dropwise to reduce the precursor. The well dispersed Vulcan XC-72R carbon was added into the sol and stirred for 2 h. The suspension was filtered, washed with deionized water, and then dried in a vacuum oven. The same procedure was used to prepare the PtAu/C catalyst by adding of $H_2PtCl_6.6H_2O$ into the Au precusor solution to obtain a nominal atomic ratio Au:Pt of 9:1. To promote alloy formation, heat treatment process was performed with a temperature range about 300-700°C at 10°C/min of heating rate under nitrogen atmosphere. The un-treated PtAu/C and thermal-treated PtAu/C with different heat treatment temperature were prepared and are designated as H-300 PtAu/C, H-500 PtAu/C, and H-700 PtAu/C

The physical and electrochemical properties of the prepared catalysts were measured. The catalytic activity and stability of the catalysts toward glycerol electrooxidation were observed using cyclic voltammetric and chronoamperometric method.

3. Results and discussion

The XRD patterns of all the heat-treated catalysts in the 2θ scan range of 20° - 90° are displayed in Fig. 1. For all the heat-treated catalysts, their XRD patterns showed a shift of 2θ corresponding to Au phase to higher values. This result indicates the formation of an AuPt alloy. The Au (220) diffraction peak was selected calculating the crystallite size because it was not affected by another Au plane so that the baseline could be drawn accurately. The lattice parameters from XRD results, as shown in Table 1, indicate that the higher heat-treatment temperature, the lower lattice parameter increasing the alloying degree Furthermore, many researchers have claimed that heat treatment is an effective method to introduce more active catalyst sites for promoting alloy formation (Bezerra et al., 2007).

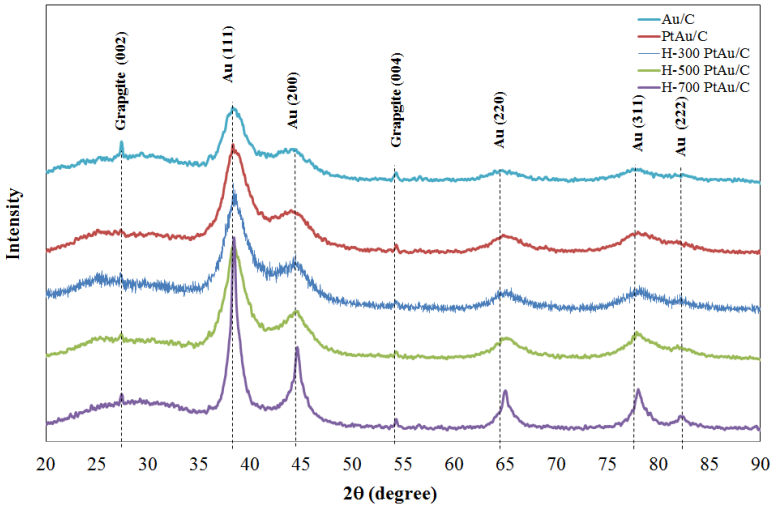

Fig.1 X-ray diffractograms of the untreated and heat-treated PtAu/C catalysts.

Table 1 Lattice parameters and crystallite sizes of untreated and heat-treated PtAu/C catalysts

Electrocatalysts	**Crystallite size$_{XRD}$ (nm)**	**lattice parameter (nm)**	**Particle size$_{TEM}$ (nm)**
Au/C	2.7	0.4065	3.94
PtAu/C	2.7	0.4048	3.81
H-300 PtAu/C	2.8	0.4047	4.23
H-500 PtAu/C	3.1	0.4044	4.85
H-700 PtAu/C	5.9	0.4043	6.04

The TEM images of the heat-treated PtAu/C catalysts are shown in Fig. 2. The effect of heat treatment temperature on metal particle sizes of the PtAu/C catalysts and their size distribution can be estimated. The size of particles was increasing with the increase of heat treatment temperature due to the sintering of the metal particles.

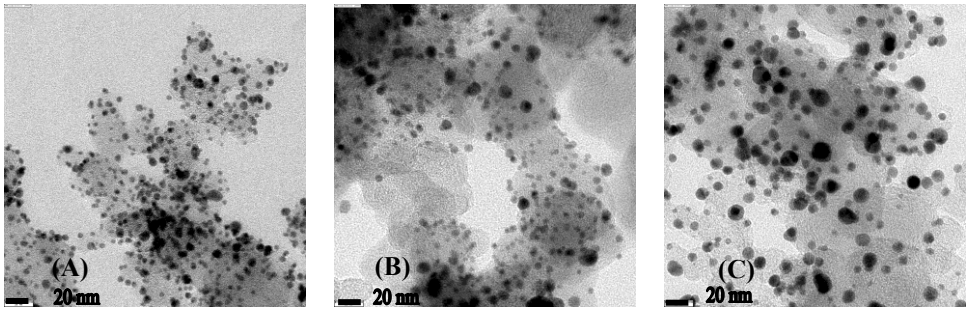

Fig. 2 TEM images particle and size distribution of the heat-treated catalysts; (A) H-300 PtAu/C, (B) H-500 PtAu/C, and (C) H-700 PtAu/C.

As shown in Table. 1, it was clearly observed that the sintering of metal particles increase with increase of temperature. The mean particle sizes of the metal particles calculated from the TEM images of all the heat-treated catalysts were in the range of 4.23-6.04 nm. These results of metal particle sizes were consistent with the XRD crystallite size.

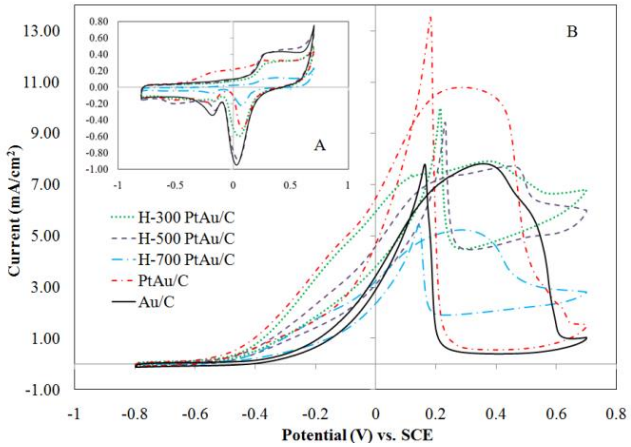

Fig. 3 CVs of the as-prepared catalysts, in 0.1M KOH (A) containing 0.1M glycerol (B).

Cyclic voltamograms (CVs) of the as-prepared catalysts in 0.1M KOH are illustrated in Fig. 3A. In the positive scan, the oxidation of the gold surface occured at around 0.2 V and in the negative scan, two reduction peaks of the reduction of the gold oxides appeared at approximately 0.05V. and -0.2V. according to the reduction of quasi-2D and quasi-3D gold oxide states (Yongprapat et al., 2012), respectively. Fig. 3B showed the CVs of the as-prepared catalysts in 0.1M KOH containing 0.1M glycerol, PtAu/C catalyst provided higher maximum current density than that of other catalysts because of the synergistic effect. Moreover, the lower of onset potential (V_{onset}) of PtAu/C might caused by the hydroxyl ion adsorbed on Pt at low potential enhance the alcohol oxidation (Yu et al., 2012).

However, the maximum current density obtained from the heat-treated catalysts was lower than the untreated PtAu/C. Among the heat-treated catalysts, the higher the heat treatment tenperature, the lower onset potential. Nevertheless, the catalyst yielding the lowest onset potential was still be the untreated PtAu/C. It was anticipated that the negative effect of the agglomeration of the catalysts particles in the heat-treated catalysts could overcome benefit obtained from the increase of alloying degree.

Table 2 The CVs and CA results from experimental data

Electrocatalysts	CVs results		CA results	
	I_{max} (mV cm^{-2})	V_{onset} (V)	δ (10^{-3}% S^{-1})	I_f (mV cm^{-2})
Au/C	7.81	-0.201	10.9	4.35
PtAu/C	10.79	-0.481	2.83	6.07
H-300 PtAu/C	7.69	-0.433	5.64	4.37
H-500 PtAu/C	7.78	-0.447	7.15	4.49
H-700 PtAu/C	5.22	-0.467	12.95	1.33

To determine the stability of these catalysts, CA experiment was conducted by holding the potential at 0.3 V. vs. SCE for 60 min in 0.1 M KOH containing 0.1 M glycerol, as shown in Fig. 4. The current produced from all catalysts drops rapidly within 2 min, and then decay slowly. After holding the potential for 60 min, final current density (I_f) and decay rate (δ) of all catalysts were measured

as concluded in Table 2. As heat-treatment temperature increased, the heat-treated PtAu/C gave a lower final current density and a higher decay rate. These results were caused by the agglomeration of the active metals as confirmed by the XRD and TEM results. Comparing the final current density, the catalyst stability of all the heat-treated and the untreated catalysts followed in descending order of PtAu/C, H-300 PtAu/C, H-500 PtAu/C, and H-700 PtAu/C, which is consistent with the results of the particle size measured from the TEM images. At the same amount of active metal, the bigger particles provided less active surface area resulting in a lower final current density. Moreover, the chronoamperometric results were in good agreement with the cyclic voltammogram results. The agglomeration of particles caused the catalyst be less active and less stable.

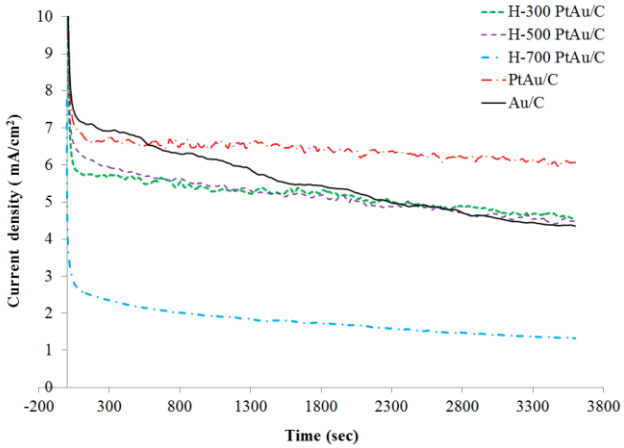

Fig. 4 CA of as-prepared catalysts, in 0.1M KOH solution containing 0.1M glycerol.

The H-700 PtAu/C catalyst which has the lowest lattice parameter (or the highest alloying tendency) exhibited the lowest decay rate. This result suggested that AuPt alloy components in the catalyst enhance its stability toward glycerol electrooxidation.

4. Conclusion

The effect of heat treatment on PtAu/C catalyst for glycerol electrooxidation in alkaline media was studies. Higher alloying degree of the heat-treated catalysts was achieved with the increase of heat-treated temperature. Consequently, the lowest onset potential of glycerol oxidation was taken place for the catalyst treated at 700°C. However, the heat treatment promoted sintering process of catalyst particle leading to the decreasing of the maximum current density. Therefore, the untreated PtAu/C showed higher performance than the heat-treated one.

5. Acknowledgement

This research work was financially supported by JGSEE. The electrochemical measurements in this research were under taken at the Fuel cell and Hydrogen Research and Engineering Center.

6. References

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