Effect of Temperature for Platinum/Carbon Electrocatalyst Preparation on Hydrogen Evolution Reaction

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Abstract. This research was carried out to study the effect of preparation temperature of the Pt/C electrocatalyst on the hydrogen evolution reaction (HER). Pt/C electrocatalyst was synthesized using the polyol method in ethylene glycol with 1 M ascorbic acid as a mild reducing agent. The investigated parameter was the temperature, which will vary from room temperature to 120°C. From the cyclic voltammetry (CV), the results showed that the Pt/C electrocatalyst synthesized by the polyol method at room temperature and 60°C cannot promote hydrogen desorption peak compared to other catalysts. The Pt/C catalyst synthesized at 100°C gave the highest electrochemical surface area (ESA) at around 32.59 m^2/g_{Pt}. From the linear sweep voltammetry (LSV) tested in an acid solution, the Pt/C catalyst synthesized at 100°C exhibited the highest HER activity. The exchange current density, Tafel slope and overpotential at 10 mA/cm^2 were around 5.208 mA/cm^2, -59.3 mV/dec and -0.277 V_{SCE}, respectively. From the value of Tafel slope: -59.3 mV/dec, it indicated that the mechanism of the 20%Pt/C electrocatalyst synthesized at 100°C catalyst occurs through Heyrovsky mechanism.

Keywords: Pt/C electrocatalyst, polyol method, ascorbic acid, hydrogen evolution.

1. Introduction

Today, there is an increasing concern over the environment and climate change due to the pollution problem. As such, an importance has been placed on the decreasing fossil fuel use due to its large contributing impact towards the global warming. Hydrogen is a renewable energy resource which can be used to produce electricity and power, which are important for sustaining human life and increase quality of living.

One of the most interesting methods used to produce pure hydrogen is the water electrolysis due to its high efficiency, carbon-free emission and simplicity of operation. Hydrogen evolution reaction (HER) is a reversible reaction of water splitting at the cathode side to produce hydrogen gas. There are three mechanisms for hydrogen gas in acid solution [1].

Volmer: $H^+ + e^- + M \leftrightarrow M\text{-}H_{ads}$ (1)

Heyrovsky: $M\text{-}H_{ads} + H^+ + e^- \leftrightarrow H_2 + M$ (2)

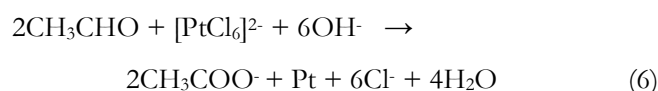Tafel: $M\text{-}H_{ads} \leftrightarrow H_2 + M$ (3)
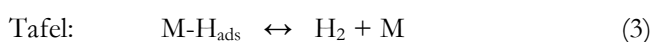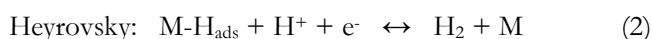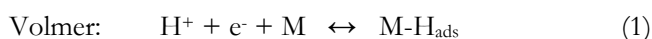
HER occurs through in 3 mechanisms: Volmer mechanisms as Eq. (1), Heyrovsky mechanism as Eq. (2) and Tafel mechanisms as Eq. (3), in an acid solution. However, HER is strongly uphill with large overpotential in some type of metal. Thus, an electrocatalyst is necessary [2]. Platinum (Pt) is the best metal for HER because of its high electrochemical properties, low overpotential and its stable in acid and basis solutions. Then Pt supported on carbon (Pt/C) is the most popular electrocatalyst for HER. It shows the best catalytic activity for HER. However, the stability and efficiency of the Pt/C catalyst was deceased with increasing of using times. Thus, a method to prepare Pt on carbon support for electrocatalyst with high stability and activity is the challenge key [3]. In the recent years, some researchers have studied the method to synthesize Pt on the supports for high active surface area, small particle and good distribution such as the impregnation [4-6], the seeding impregnation [7], the sputtering [8-10], and microwave-assisted polyol process [11-13] including the polyol method. Zignani et al. [6] prepared a Pt-Ni/C electrocatayst by $NaBH_4$ reduction through impregnation. The results demonstrated that the crystallite size of metal was around 5.9 to 6.1 nm. It also showed an excellent electrocatalyst activity for polymer electrolyte fuel cell. However, methods like this and other similar methods are often complicated, have a negative impact to environment, and require expensive equipment [14]. Moreover, some excessive water from the preparation method will lead to a poor dispersion of catalyst on the support and increasing particle size that show poor electrocatalyst activity [15].

The polyol method is now a widely recognised method for preparation of nanoparticles because it allows to control the particle size and the distribution of the catalyst on its supports. Moreover, the fact that it does not use water in the system and can easily be scaled up to a large process. The solvent that used in polyol method is different from other methods because the solvent that is used can act both as a solvent and a reducing agent at the same time without the need for water in the system. However, it requires high temperature and long time to become a reducing agent [16]. Ethylene glycol ($C_2H_4(OH)_2$) is a common solvent used in the process due to its high boiling point, capability in preventing prepared metal from oxidation and reducing metal accumulations and ability to coordinate metal with supports. Moreover, the polyol process can use a mild reducing agent such as ascorbic acid to reduce the metal ions for the reaction and the synthesis temperature. Despite the method having many advantages, it is limited for some metal precursor such as hexachloroplatinic acid ($H_2PtCl_6.6H_2O$) that is stable in solvent at room temperature [17]. The H_2PtCl_6 is a common precursor for Pt catalyst because it has a high quantity of platinum: similar to that of commercial Pt/C [18]. Through literature, Sian et al. [19] has shown that H_2PtCl_6 may coordinate with water through the hydrolysis process when alkaline is added in the solution. Water will replace some of the Cl and Pt ions to create $[PtCl_2(H_2O)_4]^{2+}$ complex. After added $NaBH_4$, $[PtCl_2(H_2O)_4]^{2+}$ is reduced to Pt without stabilizing agent that Pt will aggregation at room temperature. When using 2-propanal as a stabilizing agent, it will reduce Pt aggregation on the support Moreover, Spieker et al. [20] showed that the amount of Pt in an H_2PtCl_6 aqueous solution has a dependency on the alkaline used in the solution, which is determined by the X-ray absorption structure characterization technology. When adding alkaline, absorption peak of Pt-Cl was decreased. In contrast, absorption peak of Pt-OH was increased followed by mechanism as shown in Eq. (4).

$[PtCl_6]^{2-} + xOH^- \rightarrow [PtCl_{6-x}(OH)_x]^{2-}$ (4)

Thus, pH of solution is important to get Pt^{4+} ion from this precursor to Pt when using a reducing agent. Nevertheless, this process utilizes lots of water in the system that may lead to poor activity of the catalyst. One method which can reduce the amount of water used in the system is polyol method using ethylene glycol as a solvent and reducing agent. The reduction process of H_2PtCl_6 by ethylene glycol can be described by the following mechanisms [15]

$2HOCH_2CH_2OH \rightarrow 2CH_3CHO + 2H_2O$ (5)

$2CH_3CHO + [PtCl_6]^{2-} + 6OH^- \rightarrow$

$\qquad 2CH_3COO^- + Pt + 6Cl^- + 4H_2O$ (6)

Ethylene glycol will be decomposed to water and acetaldehyde (CH_3CHO) under heat treatment as the

reaction (5). Then acetaldehyde will reduce Pt^{4+} ion to Pt following the reaction (6). Then, the reduction of Pt is increased with increasing of acetaldehyde concentration from ethylene glycol decomposition in the reaction (5).

From reviewing the literatures, heat provided for catalyst preparation by polyol method using ethylene glycol as a solvent is an important parameter. For this reason, the main purpose of this research is to focus on effect of temperature on Pt/C electrocatalyst preparation in ethylene glycol by polyol method using ascorbic acid as reducing agent. The prepared Pt/C catalysts will be tested the electrocatalytic activities for hydrogen evolution reaction in an acidic solution.

2. Experimental

This section describes the chemicals, processes, and experiments used for the purpose of the research. All chemicals, materials, and equipment are detailed within this section.

2.1. Chemicals and Materials

The chemicals and material employed in this work are listed as following; hexachloroplatinic acid hydrate ($H_2PtCl_6.6H_2O$, Sigma-Aldrich), Pt/C commercial (20%wt, ETEK), ethylene glycol (($C_2H_4(OH)_2$, Ajax finechem), deionized water (DI-Water), Ascorbic Acid ($C_6H_8O_6$, Sigma-Aldrich), ethyl alcohol (99.99%C_2H_5OH, QRëC), hydrochloric acid (37%wt HCl, QRëC), nitric acid (65%wt HNO_3, QRëC), sulfuric acid (98%wt, H_2SO_4, QRëC), 2-propanol (99.99% C_3H_7OH, Fisher), Nafion® Solution (5%wt, Sigma-Aldrich), Carbon Powder (Vulcan XC-72, Cabot), hydrogen gas (99.999%H_2, Thai-Japan Gas), and nitrogen gas(99.999%N_2, Thai-Japan Gas)

2.2. Catalyst Preparation

2.2.1. Carbon treatment

Carbon Vulcan XC-72 powder was treated by mixing acid between 12 M of H_2SO_4 and 12 M of HNO_3 to remove the impurity before using. The volume ratio of mixing acid was 7:3 of H_2SO_4 and HNO_3, respectively [21]. The solution with carbon powder was stirred for 6 h and hold afterward for 18 h. The treated carbon was filtrated and washed by DI-water until pH equal to 4.

2.2.2. Pt/C preparation by polyol method

The 20% Pt/C was synthesized in ethylene glycol using 1 M ascorbic acid as a reducing agent at room temperatures to 120°C, respectively. Firstly, the treated carbon from section 2.2.1 was mixed with ethylene glycol and sonicated at room temperature. Secondly, 7.5 mg of Pt from $H_2PtCl_6.6H_2O$ was added into the solution and stirred at the synthesis temperature for 3 h. After stirring,

the solution was adjusted pH to 12 by adding 2 M NaOH and heated at the same temperature as the second step and stirring for 1 h. The next step, the solution was changed the pH 12 to pH 2 by adding 5 M HCl and stirring for one hour. After that, 1 M ascorbic acid was slowly added in the solution and stirred for 12 h. Finally, the solution was filtrated by ethanol alcohol until pH equal to 4 or 5 and dried for 12 h at 110°C.

2.3. Catalyst Ink Preparation and Electrochemical Measurements

2.3.1. Catalyst ink preparation

The catalyst ink was prepared by mixing 0.0125 g of prepared electrocatalyst powder in section 2.2.2 or 20% Pt/C commercial with 0.5 ml distilled water and then sonicated at room temperature for 30 min. After sonication, 0.5 ml isopropanol was added into the solution and sonicated 30 min. The last step, 0.22 ml Nafion solution was added into the solution and sonicated for 30 min before coated on the glassy carbon electrode [21].

2.3.2 Electrocatalyst characterization

Prepared electrocatlysts were analysed weight of metal by Thermogravimetric analysis (TGA) using a TG instrument: 209 F3 Tarsus, at temperatures ranging from 50 to 1000°C at heating rate 10°C/min under an oxygen atmosphere.

2.3.3 Electrochemical measurements

The electrochemical measurements were carried out at 25°C by using the three-electrode system on the Potentiostat/Galvanostat (PG STATO 30, AUTOLAB COMPANY). Glassy carbon electrode, a Pt wire and a saturated calomel electrode (SCE, $0.241V_{SHE}$) were used as the working electrode, the counter electrode and the reference electrode, respectively. The 3 μl of catalyst ink from section 2.3.1 was coated on 0.035 cm diameter of glassy carbon electrode. Before testing, the 0.5 M H_2SO_4 solution was bubbled by N_2 gas for 30 min to use as an electrolyte. The electrochemical surface area (ESA) was determined by the cyclic voltammetry (CV) in N_2-saturated acid solution. The potential was varied between -0.2 to 1.0 V_{SCE} at a scan rate 20 mV/s. For HER activities, the polarization curve by linear sweep voltammetry (LSV) was recorded in potential range -0.6 to 0.00 V_{SCE} at a scan rate of 5 mV/s with rotating speed 1500 rpm in N_2-saturated acid solution.

3. Results and Discussion

3.1. Electrochemical Characterization of Pt/C Synthesized and Commercial Catalysts

The electrochemical characterization of all catalysts was determined by CV technique at potential range -0.2 to 1.0 V_{SCE} under nitrogen gas atmosphere in acid solution as shown in Fig. 1. At the anodic scan, the peaks number (I) and (II) show hydrogen desorption peak of Pt and the peak number (III) shows adsorption hydroxide peak of Pt (Pt-OH). In contrast, the peak number (V) shows oxygen adsorption of Pt (Pt-O), the peak number (VI) and (VII) show hydrogen adsorption peak (Pt-H) at cathodic scan [22].

As shown in Fig. 2(a), the CV curves of the Pt/C synthesized at room temperature and 60°C are same as that of carbon support. It did not show the H atom adsorption/desorption peaks at the potential range of -0.2 to 0.1 V_{SCE}. So, these conditions maybe not able to well synthesize Pt metal on the carbon support to promote H adsorption/desorption peak. When increasing the temperature more than 60°C, the CV curves of catalysts are similar to that of Pt/C commercial as shown in Fig. 2(b), in that they showed the H atom adsorption/desorption peaks in the potential range of -0.2 to 0.1 V_{SCE}. This indicates that the temperature is a crucial factor to synthesize the catalyst by polyol method. This might be attributed to the fact that the Pt ions cannot reduce to Pt in ethylene glycol at temperature less than 60°C.
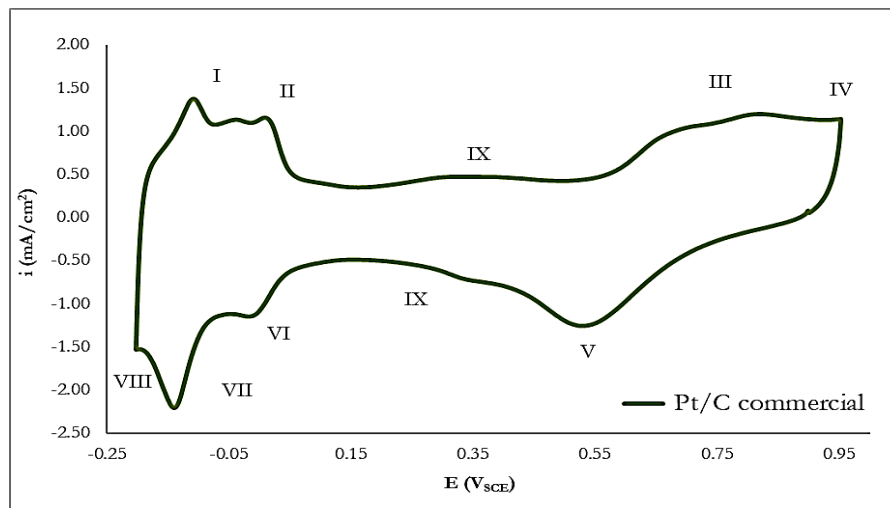

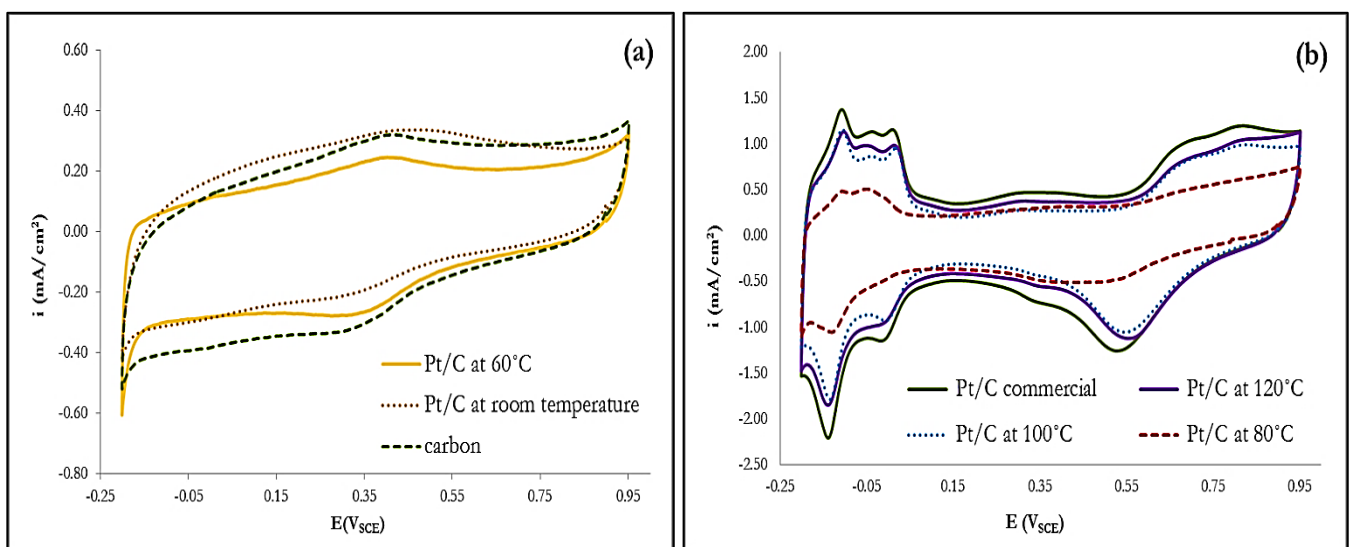Fig. 1. Cyclic voltammogram of oxidation/reduction on Pt/C commercial.

Fig. 2. Cyclic voltammograms of (a) 20%Pt/C synthesized catalysts at room temperature and 60°C and carbon (b) 20%Pt/C synthesized at 80°C, 100°C, 120°C and 20%Pt/C commercial catalyst in 0.5 M H_2SO_4 under N_2 atmosphere at scan rate 20 mV/s.

Moreover, electrochemical surface area (ESA) can calculate from area of H atom desorption followed by Eq. (7)

$$ESA = \frac{Q_H}{[M] \times 0.21} \qquad (7)$$

where Q_H is the charge for hydrogen desorption (mC/cm^2), [M] is the metal loading of Pt on the electrode (g_{Pt}/cm^2) and 0.21 is the charge required to oxidize a monolayer of H_2 on Pt [23]. From the Table 1, it can be observed that ESA increases when the preparation temperature was increased from 80 to 100°C. When increasing temperature to 120°C, the result showed that the ESA decreased. This is because the solvent in the solution was evaporated at 120 °C leading to aggregation and bad dispersion of Pt particle on the carbon support. Another reason can explain that Pt ions are fast reduced at higher temperature to give large particle size. This result is corresponding with that of Zeng et al.[15] They found that Pt ion cannot be completely reduced to Pt crystalline grains at low temperature. By contrast, at higher temperature Pt ion in solution was rapidly reduced. Then Pt crystalline grains can be aggregated, resulting for the Pt particle size. The Pt/C synthesized at 100°C exhibited the highest ESA around 32.59 m^2/g_{Pt}. However, the ESA of Pt/C synthesized at 100°C is still less than the ESA of Pt/C commercial.

Table1. ESA values of synthesized and commercial Pt/C catalysts.

Sample	ESA* (m^2/g_{Pt})
Pt/C commercial	41.90
Pt/C at 120°C	29.90
Pt/C at 100°C	32.59
Pt/C at 80°C	11.51
Pt/C at 60°C	NA
Pt/C at room temperature	NA
Carbon	NA

*ESA based on 20 mg of Pt on carbon support.

3.2. HER Activity of Synthesized and Commercial 20%Pt/C Catalysts

The HER activity of all catalysts was determined by LSV under nitrogen gas atmosphere in the acid solution at a scan rate of 5 mV/s and potential range of -0.6 to 0 V_{SCE}. The polarization curve that can determine the onset potential. The onset potential is a potential that reaction will start. Catalysts has a small value of onset potential, the reaction can rapidly occur. As shown in Fig. 3 and Table 2, it can be observed

that the Pt/C electrocatalyst synthesized at room temperature exhibited the highest onset potential closing to the carbon substrate that was around -0.240 V_{SCE}. Thus, the catalysts synthesized at room temperature needed more potential to drive the reaction to proceed. In other words, the reaction occurred slower than other catalysts synthesized at high temperature. However, Pt/C synthesized at 60°C exhibited less onset potential than the catalyst synthesized at room temperature even though no H atom desorption peak in cyclic voltammogram as shown in Fig. 2(a). So, it could confirm that very small Pt ion can be reduced at this temperature. However small amount of Pt on the support cannot detect H atom adsorption/desorption peak by CV technique. Moreover, this result is confirmed by the TGA analysis as shown in Fig. 4. It showed that Pt/C synthesized at 60°C has approximately 98% weight loss or 2%wt Pt remaining in catalyst. But catalyst synthesized at 100°C has approximately 15%wt Pt and at 120°C has approximately 13%wt Pt, respectively. Because if the temperature of heating is low (60°C), there is not enough energy to fully reduce Pt. Conversely, if energy is too high (120°C), the reduction of Pt occurs too fast and Pt nanoparticles aggregate on the support which leads to lower of the electrochemical surface area [15]. For Pt/C synthesized at 80°C, it exhibited a lower onset potential nearly the Pt/C commercial that was around -0.212 V_{SCE}. So, the onset potential reduces with increasing of temperature. The 20%Pt/C synthesized at 100°C exhibited excellent HER activity that got a small onset potential that was around -0.210 V_{SCE}.
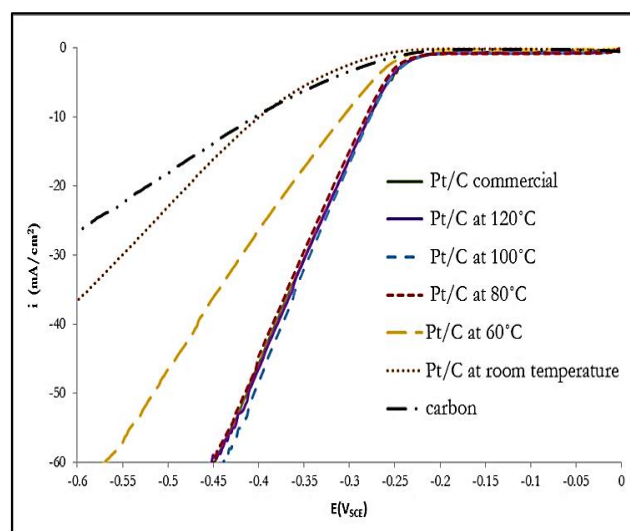

Fig. 3. Polarization curves of at room temperature, 60, 80, 100, 120 °C and Pt/C commercial and carbon catalysts in 0.5 M H_2SO_4 under N_2 atmosphere at scan rate 5 mV/s with rotating speed 1500 rpm.

Moreover, HER activity can determine by Tafel equation as shown in Eq. (8) expressed by kinetic

parameters: exchange current density (i_0), overpotential at 10 mA/cm² (η_{10}) and Tafel slope (b).

$$\log i = \log i_0 - \frac{\alpha nF}{2.303RT}\eta_{act} \qquad (8)$$

where i is current density (mA/cm²), α is the mass transfer coefficient, n is number of electron in the reaction (n = 2 for hydrogen), F is Faraday's constant (96480 C/mol), R is gas constant (J/mol K), T is absolute temperature (K) and η_{act} is activated overpotential (V) [23]. These parameters were determined by fitting the linear equation between overpotential (η) and magnitude of current density (log i) as shown in Fig. 4. The intercept was used to calculate exchange current density and the slope was used to determined Tafel slope. Exchange current density and Tafel slope were commonly used to describe the kinetic analysis of HER catalyst [24].

The Tafel plot in Fig. 5(a) and kinetic parameters in Table. 2 showed that the Pt/C synthesized at room temperature exhibited a large Tafel slope as a carbon catalyst. Which catalysts show a large Tafel slope, the catalysts need a high overpotential to increase the reaction rate. Otherwise, the exchange current density that showed the rate of reaction at equilibrium is small. The Pt/C synthesized at room temperature exhibited the highest overpotential at 10 mA/cm² of around -0.400 V_{SCE} and smallest exchange current density (2.016 mA/cm²). When increasing the synthesis

temperature, the Tafel slope and overpetential at 10 mA/cm² also decreases as shown in Fig. 5(b). The Pt/C synthesized at 100°C exhibited the highest exchange current density around 5.208 mA/cm² and smallest Tafel slope (-59.3 V_{SCE}) and lowest overpotential at 10 mA/cm² (-0.277 V_{SCE}) that is nearly 20%Pt/C commercial. Despite ESA of the catalyst synthesized at 100°C is less than 20%Pt/C commercial, the catalyst exhibited HER activity nearly commercial catalyst.
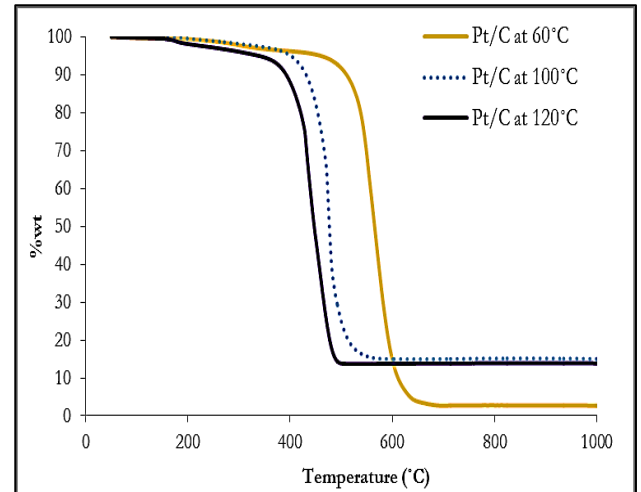

Fig.4. TGA analysis of 20%Pt/C synthesized at 60, 100 and 120°C.
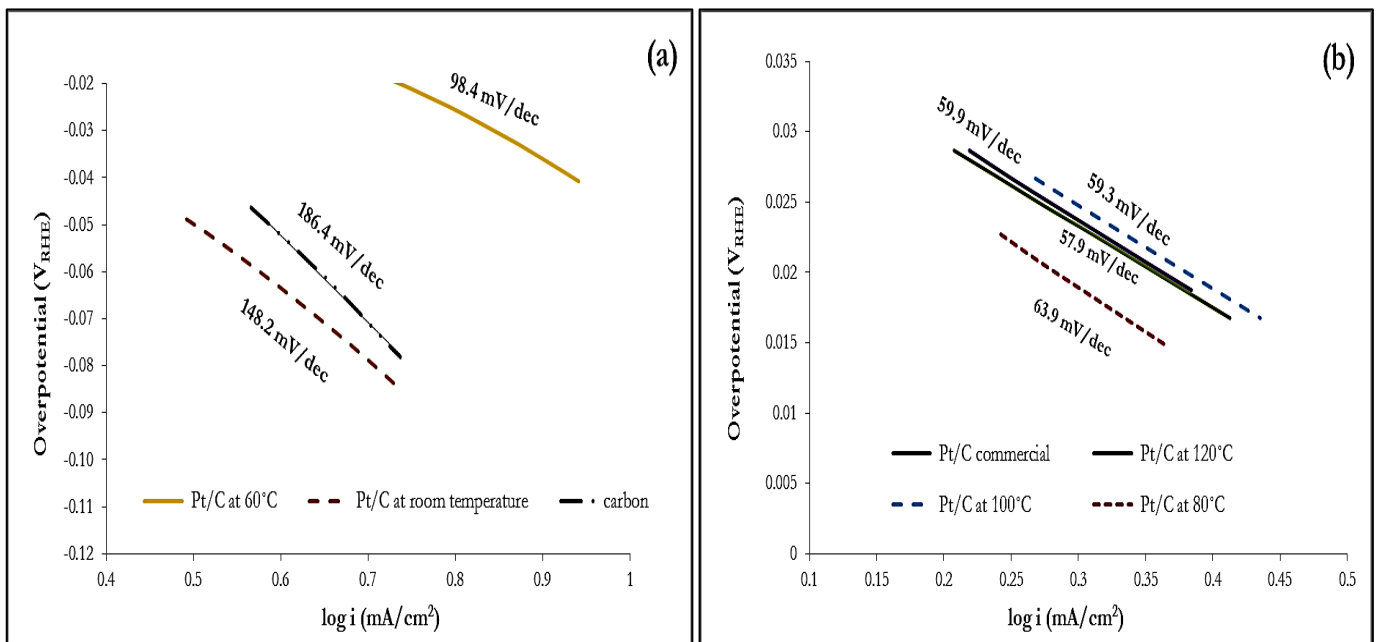

Fig. 5. Tafel plots of (a) Pt/C synthesized catalysts at room temperature and 60°C and carbon, (b) Pt/C synthesized at 80, 100, 120°C and commercial catalysts fitting by Tafel equation.

Table 2. HER parameters activities of 20%Pt/C synthesized and commercial catalysts.

Sample	Onset potential (V_{SCE})	η_{10} (V_{SCE})	b (mV/dec)	i_0 (mA/cm²)
20%Pt/C commercial	-0.216	-0.277	57.9	5.046
Pt/C at 120°C	-0.214	-0.279	59.9	4.967
Pt/C at 100°C	-0.210	-0.277	59.3	5.208
Pt/C at 80°C	-0.212	-0.285	63.9	3.947
Pt/C at 60°C	-0.234	-0.307	98.4	3.424
Pt/C at room temperature	-0.240	-0.400	148.2	1.475
Carbon	-0.239	-0.405	186.4	1.300

The Tafel plot in Fig. 5(a) and kinetic parameters in Table. 2 showed that the Pt/C synthesized at room temperature exhibited a large Tafel slope as a carbon catalyst. Which catalysts show a large Tafel slope, the catalysts need a high overpotential to increase the reaction rate. Otherwise, the exchange current density that showed the rate of reaction at equilibrium is small. The Pt/C synthesized at room temperature exhibited the highest overpotential at 10 mA/cm² of around -0.400 V_{SCE} and smallest exchange current density (2.016 mA/cm²). When increasing the synthesis temperature, the Tafel slope and overpetential at 10 mA/cm² also decreases as shown in Fig. 5(b). The Pt/C synthesized at 100°C exhibited the highest exchange current density around 5.208 mA/cm² and smallest Tafel slope (-59.3 V_{SCE}) and lowest overpotential at 10 mA/cm² (-0.277 V_{SCE}) that is nearly 20%Pt/C commercial. Despite ESA of the catalyst synthesized at 100°C is less than 20%Pt/C commercial, the catalyst exhibited HER activity nearly commercial catalyst.

Moreover, the Pt/C catalyst synthesized at 120°C exhibited an activity nearly with Pt/C commercial and showed a lower onset potential than Pt/C commercial that was around -0.214 V_{SCE}. So, the catalyst prepared by the polyol method can improve efficiency of the catalyst because it can reduce water from the reaction and increasing dispersion of catalyst on the support.

Furthermore, Tafel slope is commonly determined possible HER reaction pathway. The HER reaction pathway in acid solution occurs through in three mechanisms: Volmer mechanism, Heyrovsky mechanism and Tafel mechanism. The theoretical Tafel slope for Volmer mechanism is -120 mV/dec, Heyrovsky mechanism is -40 mV/dec and Tafel mechanism is 30 mV/dec [25]. From the Tafel slope of Pt/C synthesized at 100°C, 120°C and commercial as shown in Fig. 5 and Table 2, they were around -59.3

mV/dec, -59.9 mv/dec and -57.9 mV/dec, respectively, which were close to the theoretical Tafel slope of Heyrovsky (40mV/dec). Thus, the HER reaction of the Pt/C catalyst synthesized at different temperatures in range of 60-120°C occurred through Heyrovsky mechanism.

From the Tafel slope of Pt/C synthesized at 100°C, 120°C and commercial as shown in Fig. 5 and Table 2, they were around -59.3 mV/dec, -59.9 mv/dec and -57.9 mV/dec, respectively, which were close to the theoretical Tafel slope of Heyrovsky (40mV/dec). Thus, the HER reaction of the Pt/C catalyst synthesized at different temperatures in range of 60-120°C occurred through Heyrovsky mechanism.

4. Conclusions

The effect of temperature on the synthesis of Pt catalysts on carbon support using hexachloroplatic acid as a Pt precursor in ethylene glycol by the polyol method was studied. At temperature lower than 60°C, the CV curve showed that no H atom adsorption/desorption peaks. Thus, this condition cannot synthesize Pt/C catalysts. However, the CV curves exhibited the H atom adsorption /desorption peaks when the preparation temperature was greater than 60°C. The synthesized Pt/C electrocatalyst at 100°C exhibited an excellent ESA and HER activity nearly that of Pt/C commercial catalyst and also can reduce amount of the Pt metal on carbon support more than other temperatures (15% wt Pt). Therefore, it could be observed that the synthesis temperature has also influence on the electrocatalytic activity for synthesized Pt/C catalyst by the polyol method using mild reducing agent as ascorbic acid. The synthesis temperature at 100°C is suitable temperature to

synthesize the Pt electrocatalyst by the polyol method for improving efficient Pt/C on HER activity.

Acknowledgement

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Uraiwun Phungjit, photograph and biography not available at the time of publication.

Mali Hunsom, photograph and biography not available at the time of publication.

Kejvalee Pruksathorn, photograph and biography not available at the time of publication.