CHAPTER 4 RESULTS AND DISCUSSIONS

4.1 Au deposition

In preparing 20 wt% of Au/C, the filtrate obtained after the immobilization step was cleared. On the other hand, for the case of 30 and 40 wt% of Au/C, the filtrate still had ruby-red color indicating that there was Au sol left in the solution. The adsorption of gold on carbon was then checked by AAs analysis of the filtrate.

Therefore, these filtrates were checked by AAs to determine the amount of Au which was deposited on carbon. The results of AAs are shown in Table 4.1. After obtaining the AAs results, the percentage of Au deposited on carbon support was calculated by using equation (3.1) to (3.3) in Chapter 3.

Table 4.1 Results of AAs and the percentage of Au deposition on carbon

Sample	**AAs$_{\text{result}}$ (mg/L)**	**% Au$_{\text{deposited}}$**
PVA method		
20% Au/ untreated C	n.d.	20.00
20% Au/ treated C	n.d.	20.00
30% Au/ treated C	11	27.81
40% Au/ treated C	48.2	27.35
Citrate method		
20% Au/ untreated C	n.d.	20.00
20% Au/ treated C	n.d.	20.00
30% Au/ treated C	0.47	29.80
40% Au/ treated C	5.9	37.11

n.d. = not detected at the detection limit of 2.0 ppm.

For 20 wt% Au/C catalyst, all of Au sol was adsorbed on carbon. However for 30 wt% and 40 wt% Au/C catalysts from both PVA and citrate methods, Au sol was not totally adsorbed on carbon. These results corresponded to the color intensity of solution observed in the catalyst preparation step.

For PVA protection method, at 30 wt% and 40 wt% Au, the percentage of Au deposition was approximately 27%. This indicated the maximum Au that could be adsorbed on carbon support. The reasons why Au sol remained in the solution were either the excessive amount of PVA or the saturation of Au adsorption on the carbon. In principle, PVA anchored with Au sol as organo-shell could prevent the agglomeration of Au particles. Since we controlled the PVA:Au ratio, the amount of PVA increased with increasing % Au. As a result of a large amount of PVA prevent in solution, active carbon could not adsorb these sol. Au sol still remained in the solution was probably caused either by the excessive amount of PVA or by the saturation of Au adsorbed on carbon. In other words, big organo-shell could interface with each other as well as with the support and inhibit the adsorption of sol on carbon surface.

For citrate protection method, at 30 wt% and 40 wt% Au, the percentage of Au deposition was more than 27 %. It shows that the Au deposition by the citrate protection method was higher than that of the PVA protection method.

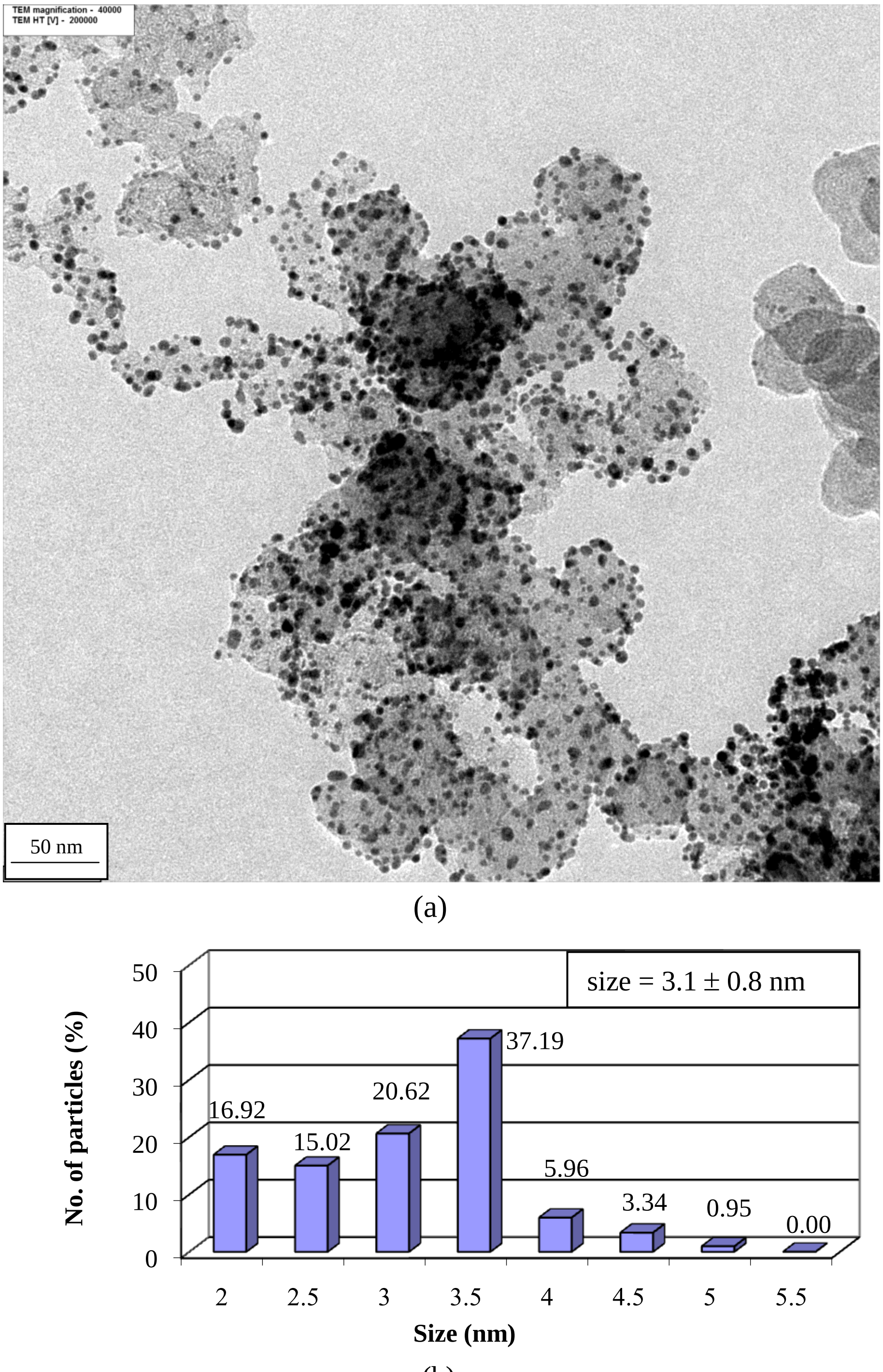
4.2 Particle Size and Size Distribution from TEM image

The particle size and size distribution was evaluated from TEM image. TEM images of catalysts by PVA protection method are shown in Figure 4.1-4.4. Figure 4.1(a) shows TEM image of 20 wt% Au catalyst by PVA protection method on untreated carbon. From Figure 4.1(b), the average Au particle size of this catalyst was approximately 3.1 ± 0.8 nm. There is a few number of Au particles with a diameter larger than 3.5 nm that are bigger than 3.5 nm. That was about 10.25%.

TEM image of the 20 wt% Au catalyst by PVA protection method on treated carbon is shown in Figure 4.2(a). From Figure 4.2(b), it was found that the average Au particle size of this catalyst was about 2.7 ± 0.5 nm. The Au particle size of this catalyst was the smallest among the prepared catalysts. Most Au particle size of this catalyst was 2.5 nm. The number of Au particles with D_p > 3.5 nm was very small accounted for 1.87 %. By comparing this catalyst with the previous one, the treated carbon provided smaller Au particle size.

Figure 4.3(a) shows TEM image of 30 wt% Au catalyst on treated carbon. For Figure 4.3(b), the average Au particle size of this catalyst was about 3.2 ± 0.6 nm. Maximum population of Au particles of this catalyst had a diameter of 3.5 nm and there was about 10.42% of Au particle with a size over 3.5 nm. At 20 wt% Au, the number of Au particles with a diameter of 3.5 nm on the treated carbon was higher than that on the untreated carbon.

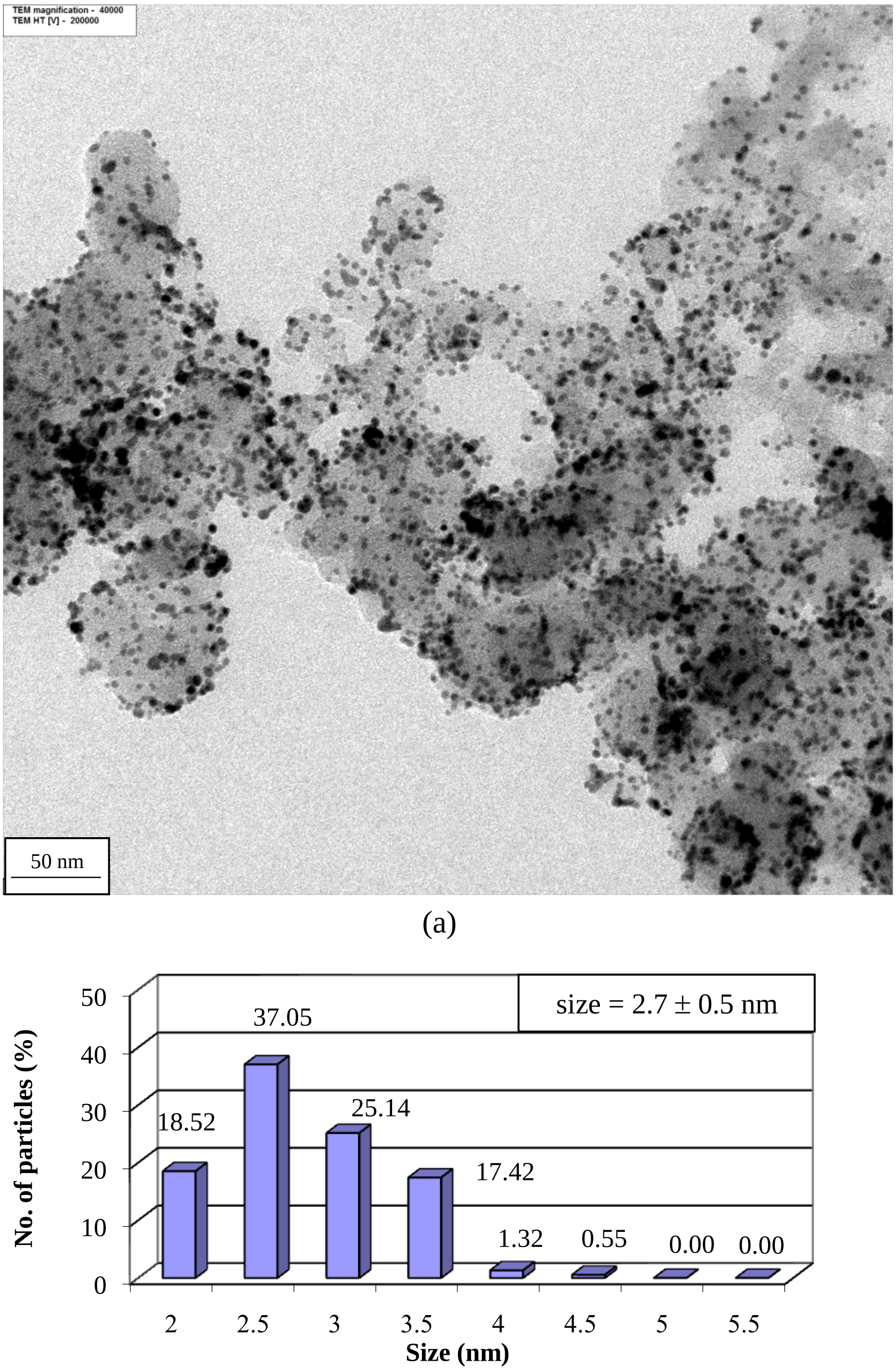
Lastly, Figure 4.4(a) shows TEM image of 40 wt% Au on treated carbon. From Figure 4.4(b), the average Au particle size of this catalyst was about 3.4 ± 0.7 nm. The Au particle size and distribution of 40 wt% /treated C was similar to that of 30 wt% Au /treated C, except that the number of Au particle with a size over 3.5 nm of 40 wt% /treated C became relatively greater than that of 30 wt% Au /treated C (23.45% compared to 10.42%, respectively). It indicated that the increase of Au loading promoted the catalyst agglomeration.



(a)

(b)

Figure 4.1 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 20% Au prepared by PVA protection method on untreated Vulcan XC-72R carbon



(a)

(b)

Figure 4.2 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 20% Au prepared by PVA protection method on treated Vulcan XC-72R carbon

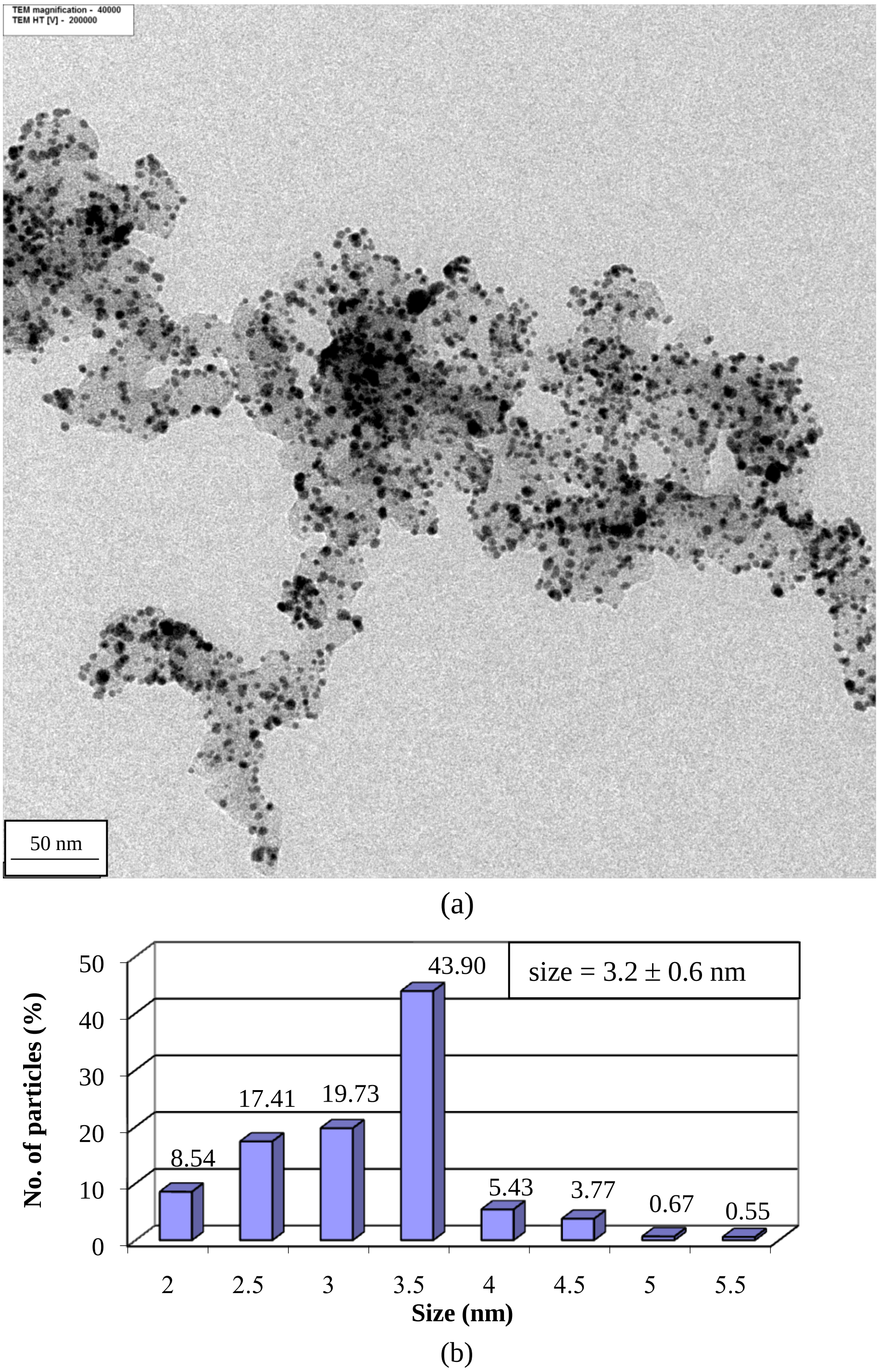
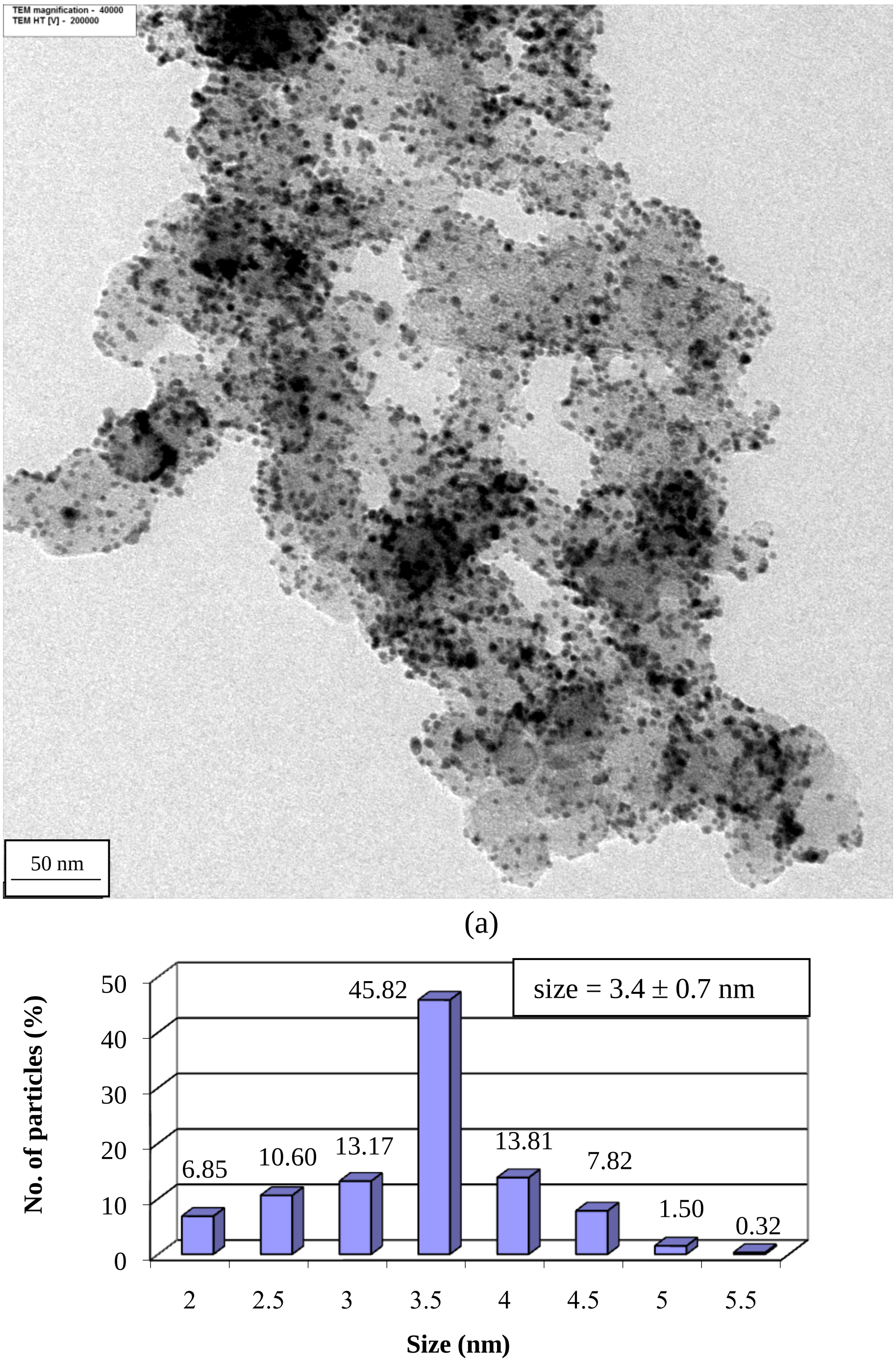


Figure 4.3 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 30% Au prepared by PVA protection method on treated Vulcan XC-72R carbon



(a)

(b)

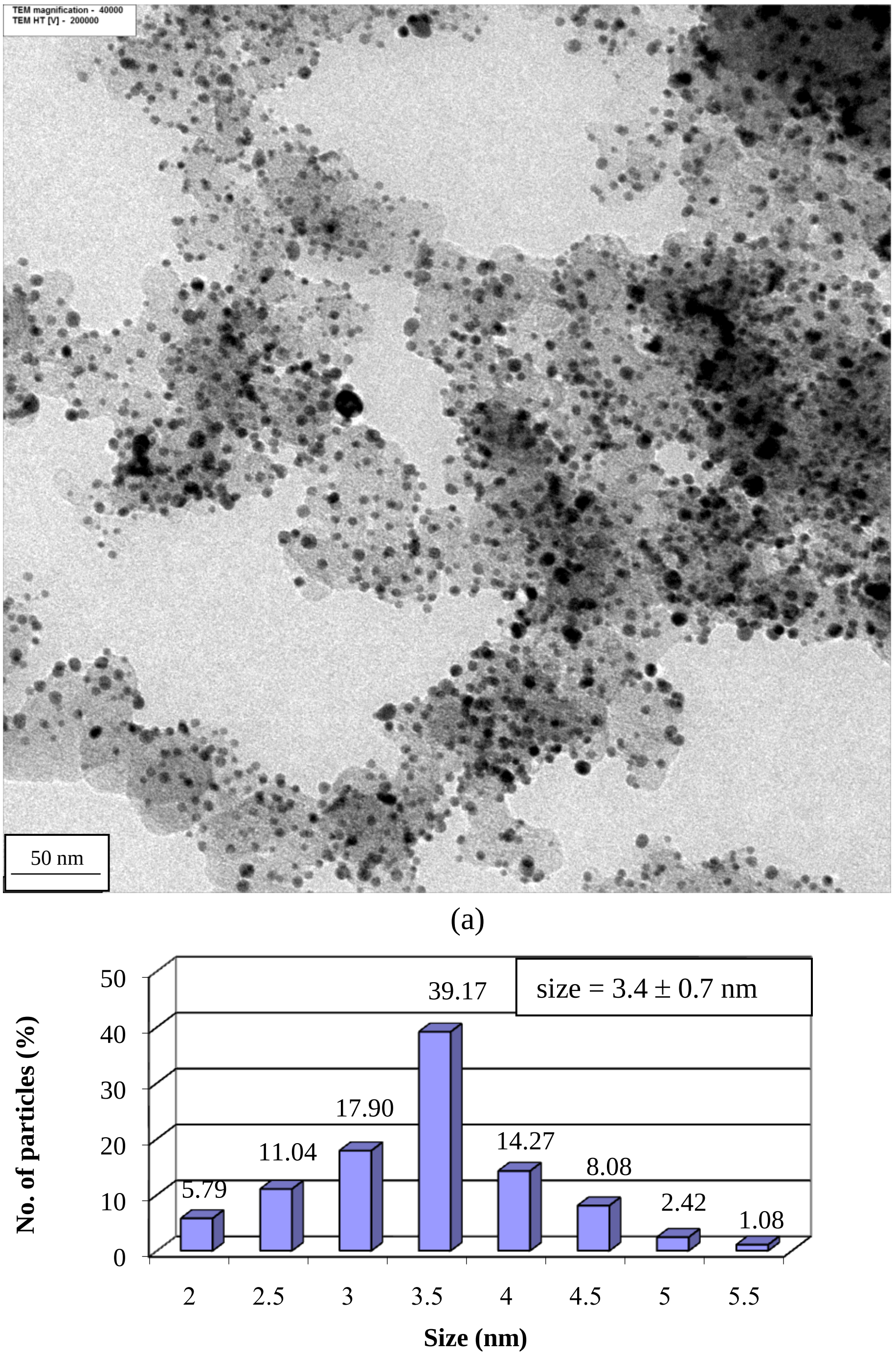
Figure 4.4 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 40% Au prepared by PVA protection method on treated Vulcan XC-72R carbon

For citrate protection method, TEM images are shown in Figures 4.5-4.8. Figure 4.5(a) shows TEM image of 20 wt% Au on untreated carbon. From Figure 4.5(b), the average Au particle size of this catalyst was approximately 3.4 ± 0.7 nm. Most of the Au size of this catalyst was 3.5 nm.

Figure 4.6(a) and (b) show TEM image and histogram of particle size distribution of the 20 wt% Au on treated carbon, respectively. The average Au particle size of this catalyst was approximately 3.3 ± 0.8 nm. The average Au particle size of this catalyst was the smallest when it was compared with the others. However, the number of the particle with the particle size < 3.5 nm was greater than that on untreated carbon. It indicated that the pretreatment of carbon support generated smaller particles. The same results was also observed in the case of PVA protection method.

Figure 4.7(a) shows TEM image of the 30 wt% /treated carbon catalyst. The particle size distribution of this catalyst as displayed in Figure 4.8(b) was then used to estimate the average Au particle size which was found to be equal to 3.4 ± 0.8 nm. Most Au particle had a diameter about 3.5 nm.

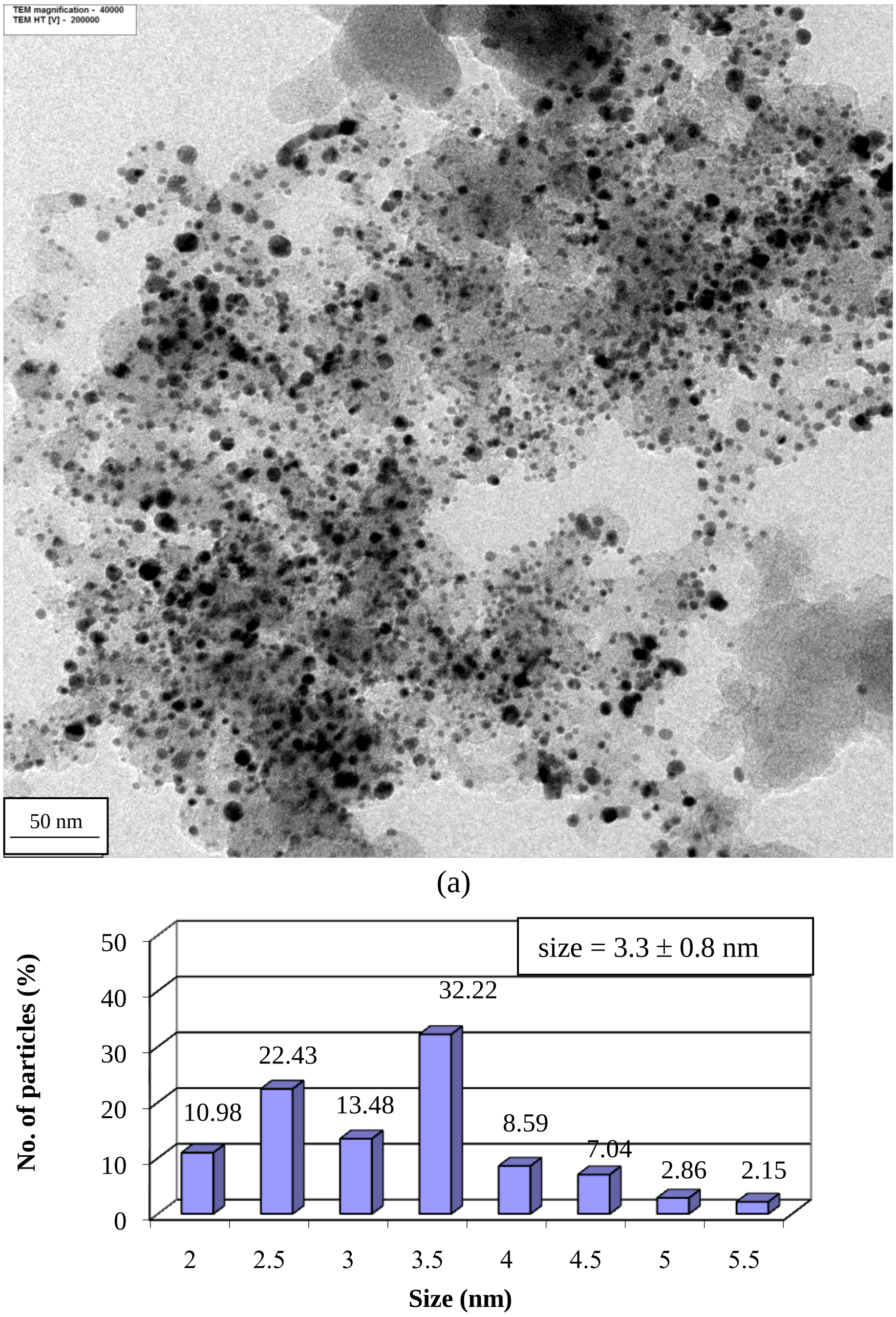
Figure 4.8(a) shows TEM image of the 40 wt% Au catalyst with treated carbon. Figure 4.8(b) shows that the average Au particle size of this catalyst was about 3.6 ± 0.9 nm. The average Au particle size of this catalyst was the biggest among all catalysts prepared by the citrate protection method. Furthermore the number of Au particles that bigger than 3.5 nm was the highest. In agreement with the PVA protection method, the number of higher particle size was increased, when the amount of Au was increased.



(a)

(b)

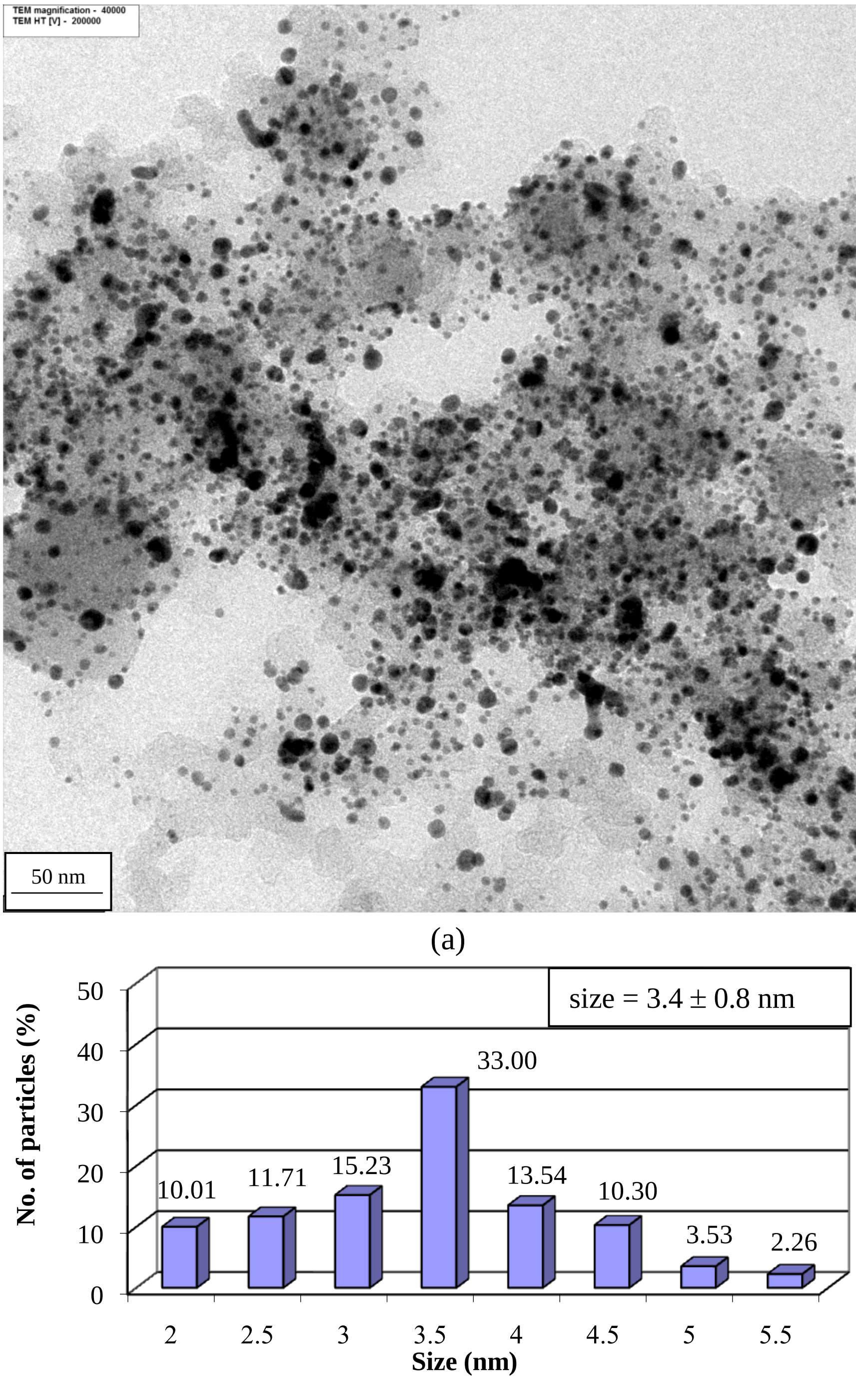
Figure 4.5 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 20% Au prepared by citrate protection method on untreated carbon



(a)

(b)

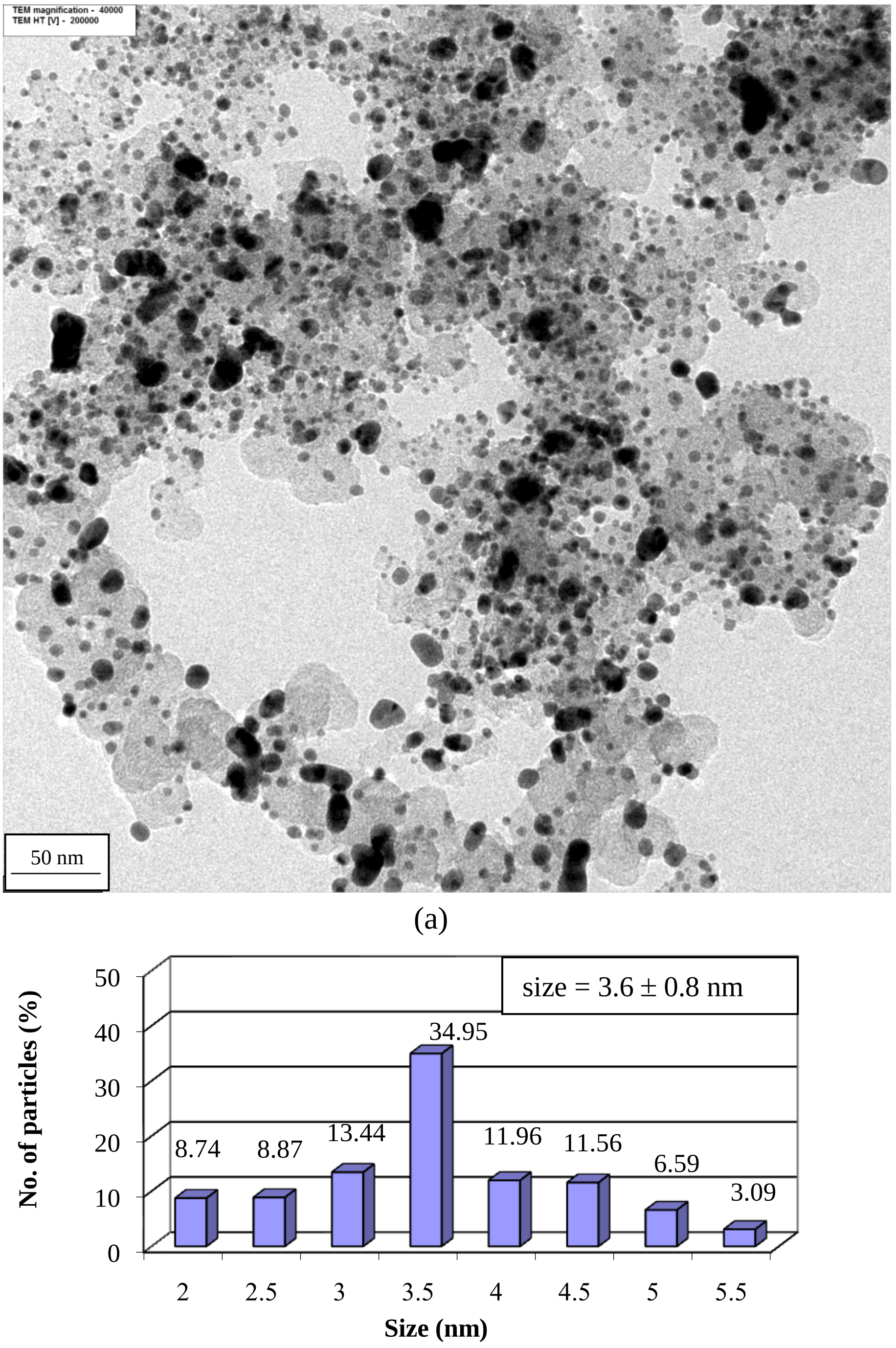
Figure 4.6 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 20% Au prepared by citrate protection method on treated carbon



(a)

(b)

Figure 4.7 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 30% Au prepared by citrate protection method on treated carbon



(a)

(b)

Figure 4.8 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 40% Au prepared by citrate protection method on treated carbon

Table 4.2 summarizes the average particle size and size distribution of each catalyst obtained from Figures 4.1-4.8. By comparing between the 20 wt% Au on treated carbon and than that on untreated carbon prepared by the same method, the treated carbon provided smaller particle than the other. From previous study [8] it was found that heat treatment of carbon support could enhance specific surface area of carbon by generating more micropores and produced less stable oxygen complexes on carbon surface. Thus, the treated carbon supports reduce the Au particle size.

For each catalyst preparation method, when amount of Au loaded was increased, Au particle size was increased. Because of increasing amount of Au, Au particles have short interparticle distances and could easily aggregate. Furthermore, from Table 4.2, it is seen that almost all Au particle sizes and size distributions of the catalyst prepared by citrate protection method was higher than that was prepared catalyst by PVA protection method.

Table 4.2 Summary of average particle size and size distribution of each catalyst

Catalyst	**Average Particle Size (nm)**
PVA method	
20% Au/ untreated C	3.0 ± 0.8
20% Au/ treated C	2.7 ± 0.5
30% Au/ treated C	3.2 ± 0.6
40% Au/ treated C	3.4 ± 0.7
Citrate method	
20% Au/ untreated C	3.4 ± 0.7
20% Au/ treated C	3.3 ± 0.8
30% Au/ treated C	3.4 ± 0.8
40% Au/ treated C	3.6 ± 0.9

4.3 Cyclic Voltammetry (CV)

In order to study the electrochemical properties of catalyst, all of Au catalyst was tested by cyclic voltammetry. Three solutions were used as the electrolytes namely 0.1M KOH, 0.1M KOH with 0.1M glycerol and 0.1M KOH with 0.1M ethylene glycol.

4.3.1 Cyclic Voltammetry (CV) in 0.1M KOH

Before testing with alcohol, each electrode was tested in 0.1M KOH to determine its electrochemical surface area (ESA). Thus there were two sets of cyclic voltammograms in 0.1M KOH which were cyclic voltammograms of all catalysts before testing with glycerol (denoted by set No. 1) and cyclic voltammograms of all catalysts before testing with ethylene glycol (denoted by set No. 2).

Figures 4.9-4.12 show the cyclic voltammograms of both Au/C catalysts prepared by PVA protection method and citrate protection method of set 1. The formations of the oxide monolayer of most catalysts commenced at about -1.7 V. At higher potential (> 0.25 V) the gold oxidation was formed according to the following reactions [7, 16];

$$Au + OH^- \rightarrow Au—OH + e^- \qquad (4.1)$$

$$Au—OH + 2OH^- \rightarrow Au(OH)_3 + 2e^- \qquad (4.2)$$

On the negative sweep, Au oxide begins to reduce at 0.3 V for the first reduction peak in which is mainly reduced from monolayer of outer surface and at about 0.01-0.02 V for the second peak which is from inner layer. The reactions on the negative sweep which are oxygen and $Au(OH)_3$ reduction are the reverse reaction of equations (4.2) and (4.1) as following [7, 16];

$$Au(OH)_3 + 2e^- \rightarrow Au—OH + 2OH^- \qquad (4.3)$$

$$Au—OH + e^- \rightarrow Au + OH^- \qquad (4.4)$$

However, the first peak of negative sweep was used to determine ESA of the catalysts because it represents the oxygen reduction. From Figures 4.9 and 4.10, the reduction peak areas of catalysts with treated and untreated carbon were close although Au/C catalyst with untreated carbon had bigger particle size. It means that the activity of the catalyst with untreated carbon in alkaline solution was nearly the same as that with treated carbon. The heat treatment on carbon support had no influence on oxygen reduction on catalyst surface in alkaline solution.

Figures 4.11 and 4.12 show cyclic voltammograms of 20 wt%, 30 wt% and 40 wt% on treated carbon prepared by the PVA protection method and the citrate protection method (set 1), respectively. The Figures show that when the amount of gold was increased, the reduction peak decreased. It may explain in terms of particle size. When the amount of gold was increased, the particle size increased resulting in less catalytic activity in alkaline solution.

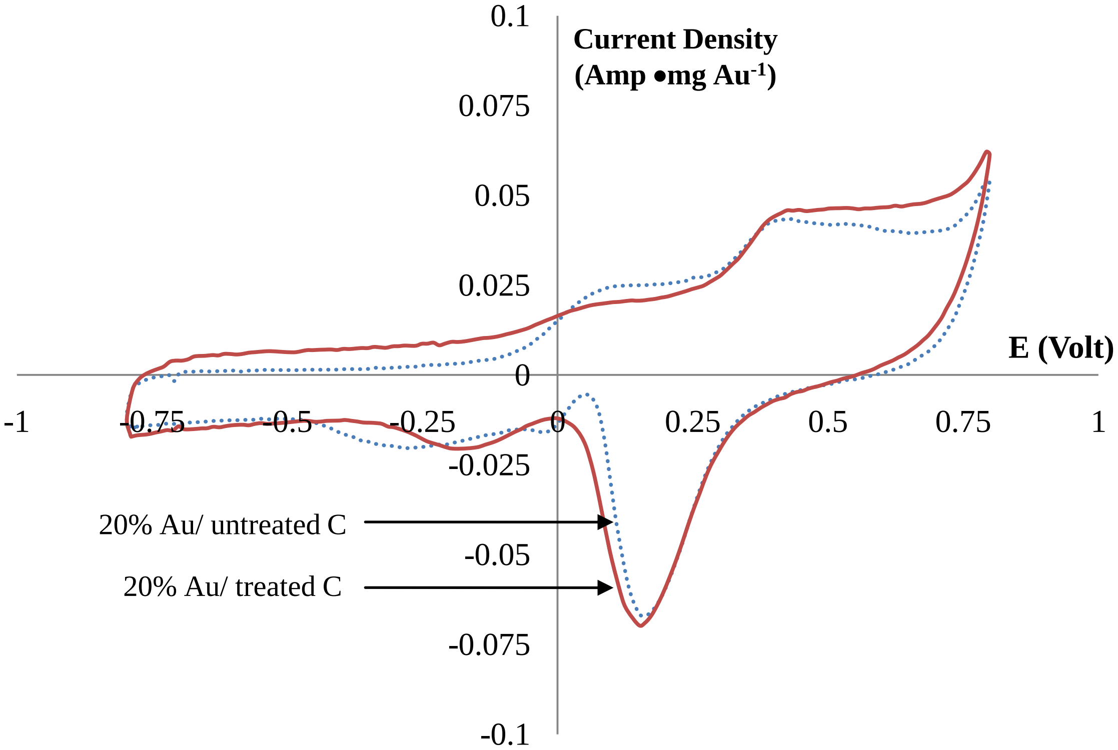


Figure 4.9 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 1)

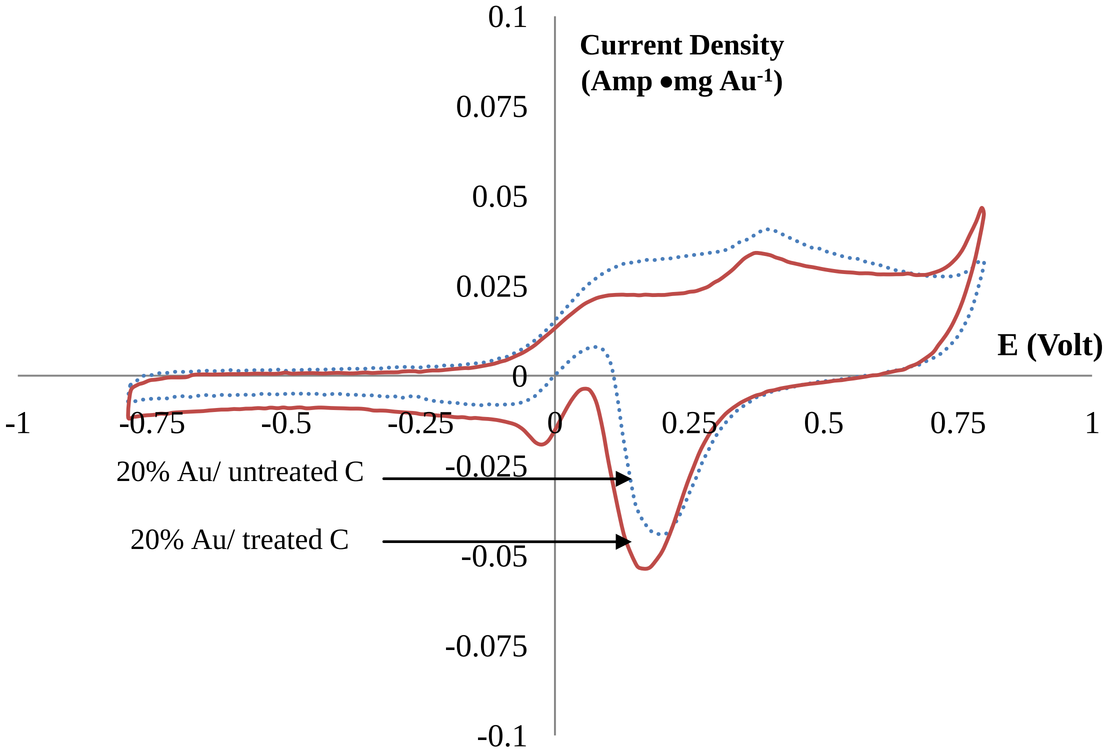


Figure 4.10 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 1)

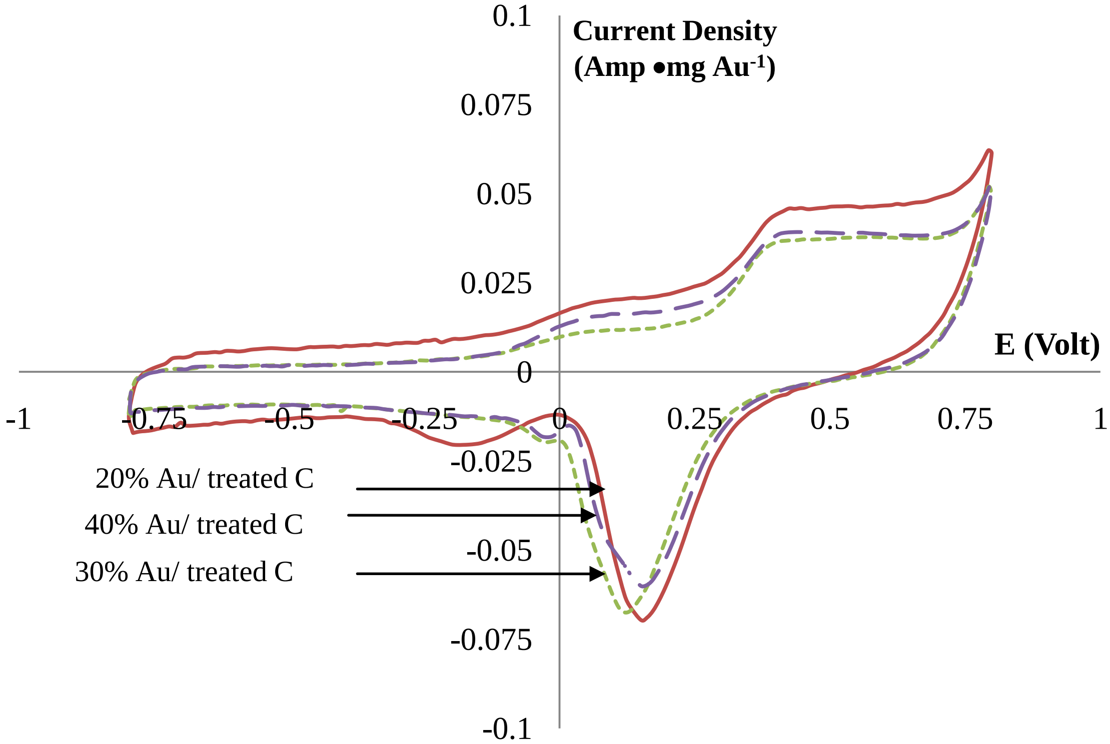


Figure 4.11 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 1)

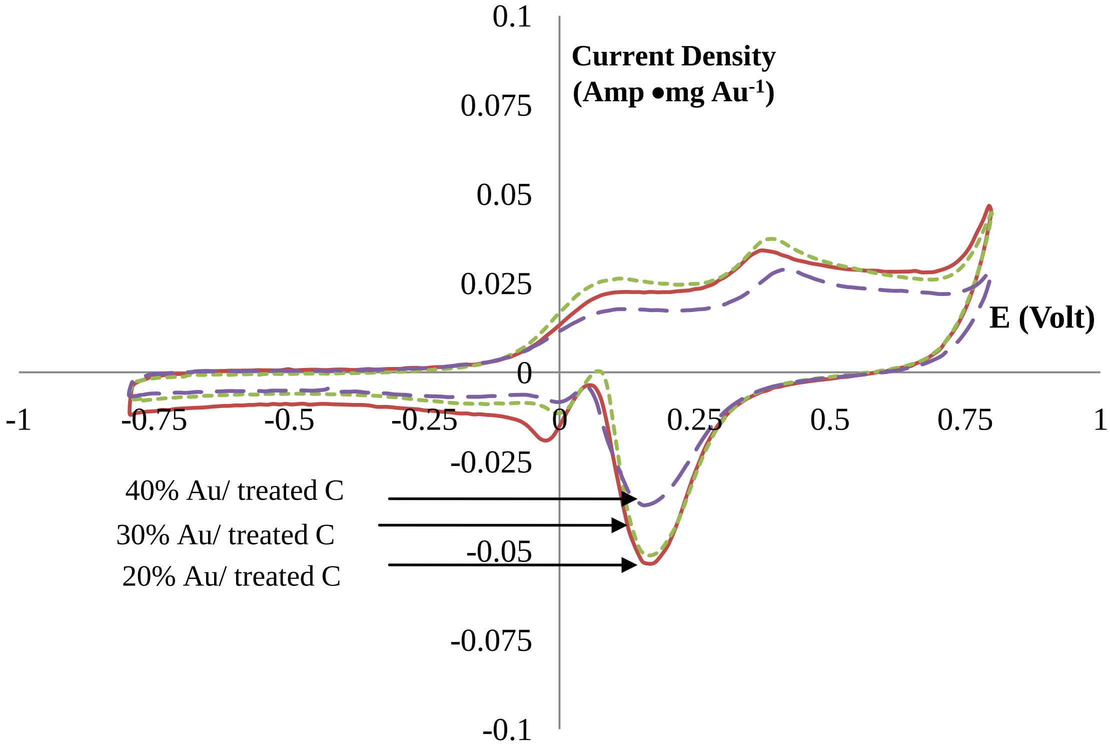


Figure 4.12 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 1)

Figures 4.13-4.16 show the cyclic voltammograms of Au/C catalysts prepared by the PVA protection method and the citrate protection method. The formation of the oxide monolayer and reduction of Au oxides commences nearly the same as that of experimental set No.1. The reactions on the positive and negative sweep were described as the above reactions. The results in Figure 4.13 and 4.14 show the same trend as that in Figure 4.9 and 4.10. The reduction peak areas of catalyst with treated carbon support and untreated carbon support were similar. It was confirmed that the oxide reduction of Au/C catalyst in alkaline solution was not affected by the pre-heat treatment of carbon support.

The results in Figures 4.15 -4.16 were similar to those in Figures 4.11-4.12. The decrease of catalytic activity of Au/C as the amount of Au loading increased resulted from the agglomeration of Au particles to form bigger particle size.

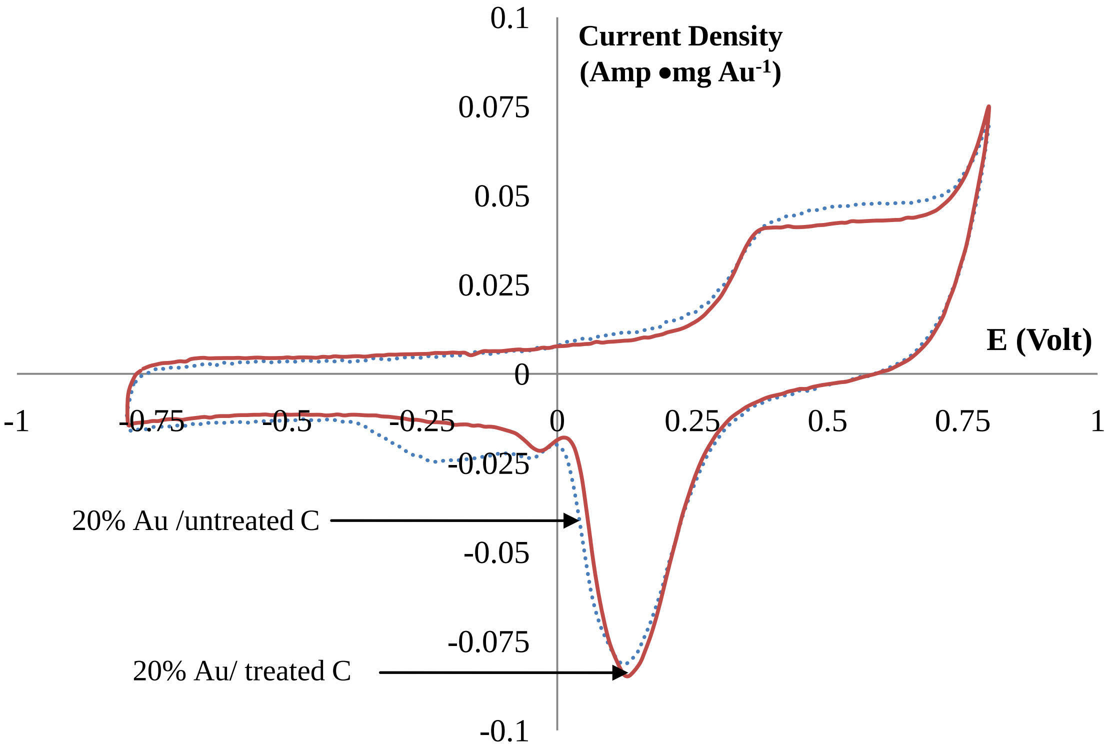


Figure 4.13 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 2)

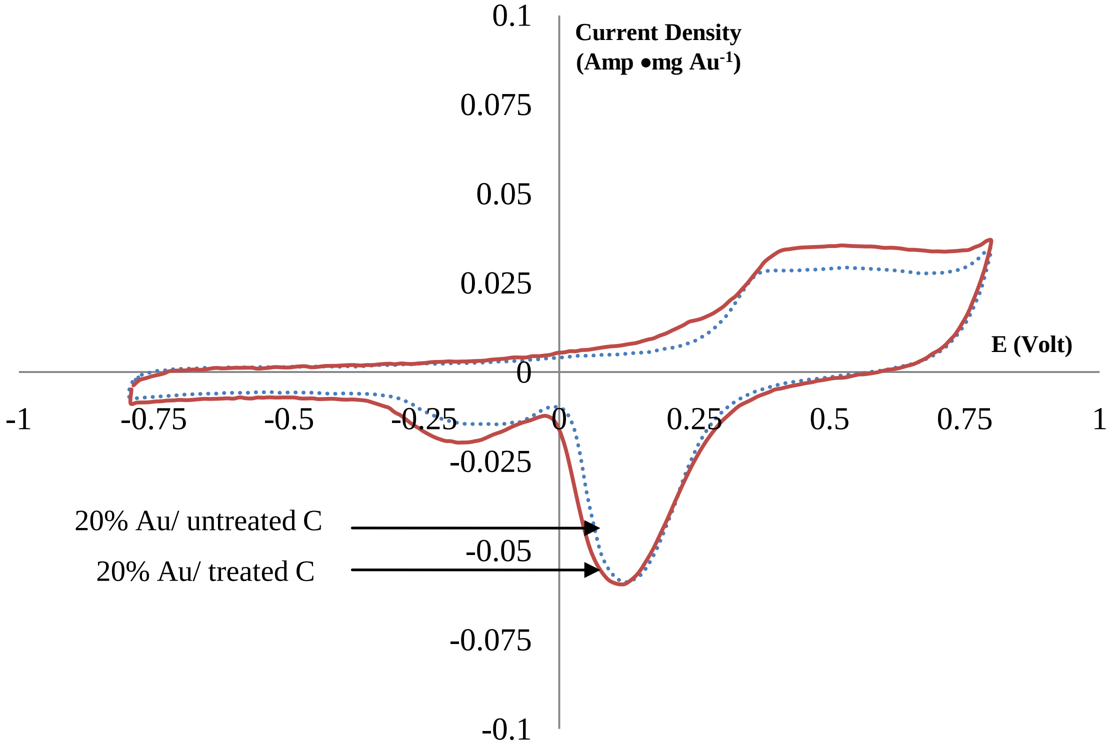


Figure 4.14 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 2)

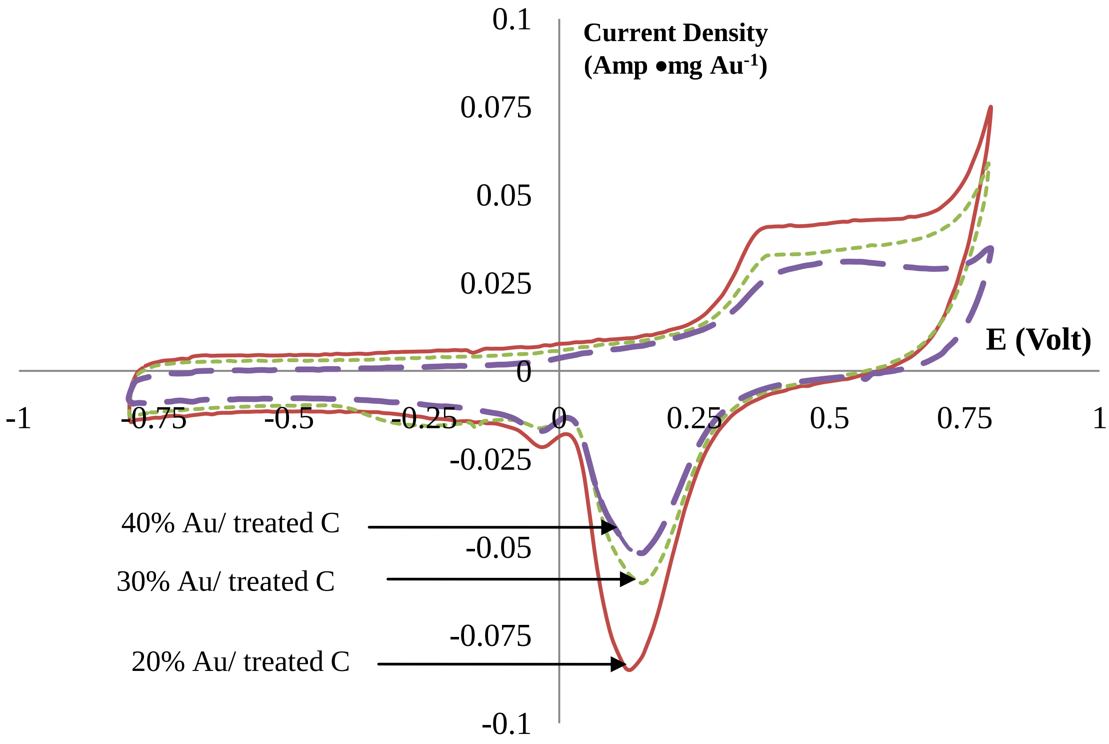


Figure 4.15 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 2)

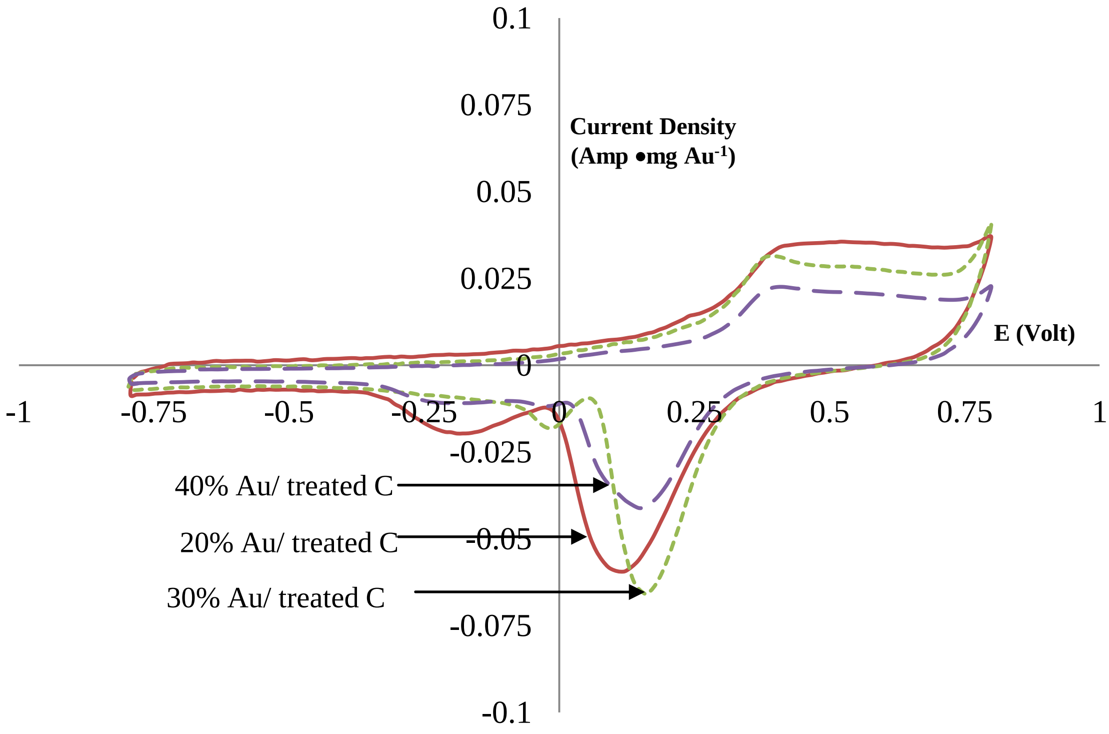


Figure 4.16 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 2)

Table 4.3 shows the ESA and average ESA which were calculated by integrating the first reduction peak of all catalysts from the experimental sets No.1 and No.2. For both PVA and citrate protection methods, the average ESAs of 20 wt% Au on treated carbon and untreated carbon were very close. Thus, as mentioned before, it can be concluded that heat treatment on carbon support did not affect oxygen reduction of the catalyst surface in alkaline solution.

For 20 wt%, 30 wt% and 40 wt% Au of Au/C catalysts prepared from both PVA and citrate protection methods, the increase of Au amount led to a decrease of ESA. The reasons were the same as described with Figures 4.11-4.12 and 4.15-4.16. Thus it can be concluded that due to the increase of particle size in accordance with the amount of Au, the bigger particle size, the lesser will be the catalytic activity in alkaline solution.

Furthermore the average ESA of the catalyst prepared by the PVA protection method is higher than that prepared by the citrate protection method. These results are in agreement with the results of TEM. The Au/C catalysts prepared by the PVA protection method had higher ESA than those prepared by the citrate protection method since the former contained smaller Au particle sizes.

Table 4.3 ESA and average ESA of Au/C catalysts prepared from both the PVA and citrate protection methods

	ESA (set 1) (m^2-Au/g-Au.)	ESA (set 2) (m^2-Au/g-Au.)	ESA_{ave} (m^2-Au/g-Au.)
PVA method			
20% Au/ untreated C	35.81	37.45	36.63
20% Au/ treated C	33.75	36.62	35.18
30% Au/ treated C	28.01	27.07	27.54
40% Au/ treated C	26.69	21.87	24.28
Citrate method			
20% Au/ untreated C	27.88	30.87	29.37
20% Au/ treated C	27.40	31.80	29.60
30% Au/ treated C	26.92	28.76	27.84
40% Au/ treated C	19.75	18.57	19.16

4.3.2 Cyclic Voltammetry (CV) in 0.1M KOH with 0.1M glycerol

As shown in Figures 4.17 to 4.20, the cyclic voltammograms of all Au/C catalysts in glycerol with alkaline solution demonstrates that there were two oxidation peaks; i.e. forward oxidation peak and reverse oxidation peak. The forward oxidation peak commenced at the potential about -0.3 V and reached the highest peak at the potential about 0.4 V. Then oxidation occurs again in the backward sweep at the potential about 0.2 V. It can be explained that the electrooxidation of glycerol commences in the potential lower than Au oxide forming region during the positive sweep (see Figure 4.9 to 4.12). When monolayer of oxide film begins, oxidation of glycerol was inhibited from the potential of 0.4 to 0.8 V. During the negative sweep, glycerol began again at the potential that the monolayer of oxide had reduced starting from 0.45 V (also see Figure 4.9 to 4.12). Generally, organic compounds are oxidesed in the presence of AuOH formed in the premonolayer region.

Since alcohol oxidation the main is reaction in fuel cell, the current density at the peak of positive sweep was used to evaluate the activity of Au/C catalyst. Form Figures 4.17 and 4.18, the catalysts with treated carbon gave higher current density than these with untreated carbon although their ESA were similar. It is possible that the gold oxide was not responsible for glycerol oxidation. Instead, the major factor was the gold particle size. The smaller particle size of catalyst yielded higher current density of glycerol oxidation. Thus, it can be concluded that the influence of particle size was higher than the presence of gold oxide (AuOH) formed on gold electrode surface.

Figures 4.19 and 4.20 show cyclic voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon prepared by the PVA and the citrate protection method. When the amount of Au increased, the current density (Amp/mgAu) was reduced. These results correspond to the previous studies [18]. The average particle sizes of 30 and 40 wt% Au catalyst prepared by the PVA protection method were about 3.2 ± 0.6 and 3.4 ± 0.7 nm, respectively, whereas they were about 3.4 ± 0.8 and 3.6 ± 0.9 nm for case of the citrate protection method. The higher of current density obtained from the 30 wt% Au/C than that from the 40 wt% Au/C corresponded to the Au particle size instead of ESA. These results confirm that the main influence of glycerol oxidation was particle size of the catalysts. However, for 20 wt% Au catalyst, both particle size and the presence of gold oxide on gold electrode surface from ESA yielded higher current density than the other catalysts.

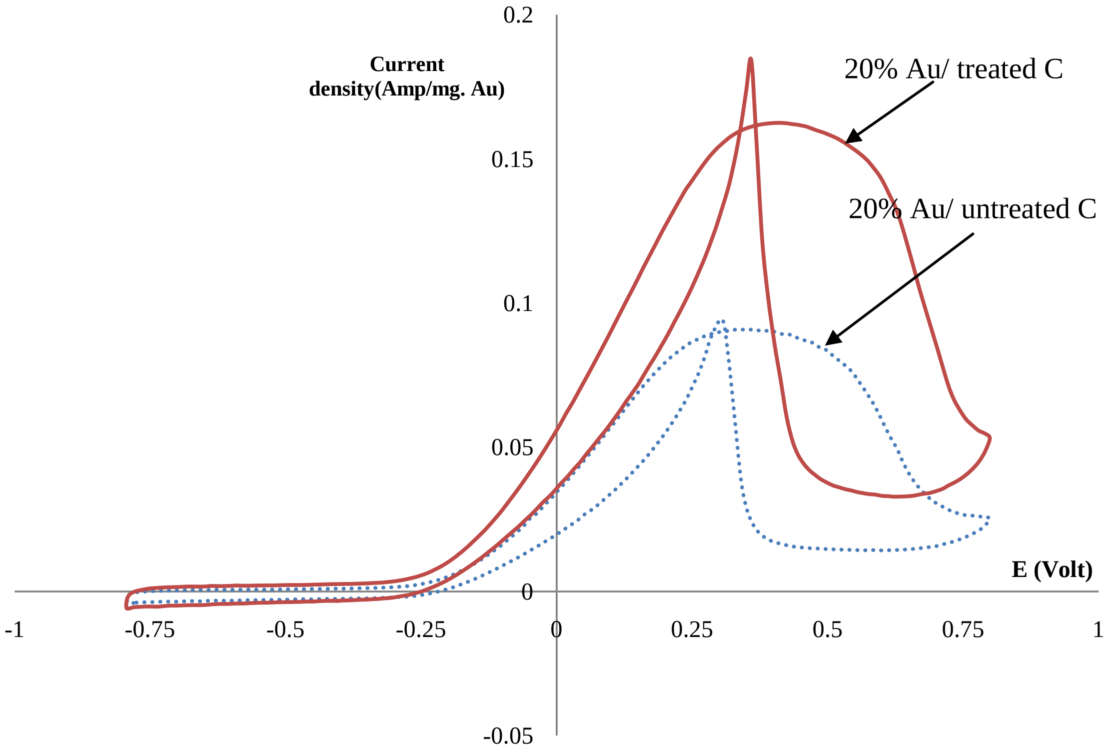


Figure 4.17 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M glycerol, scan rate 20 mVs^{-1} at 25 °C

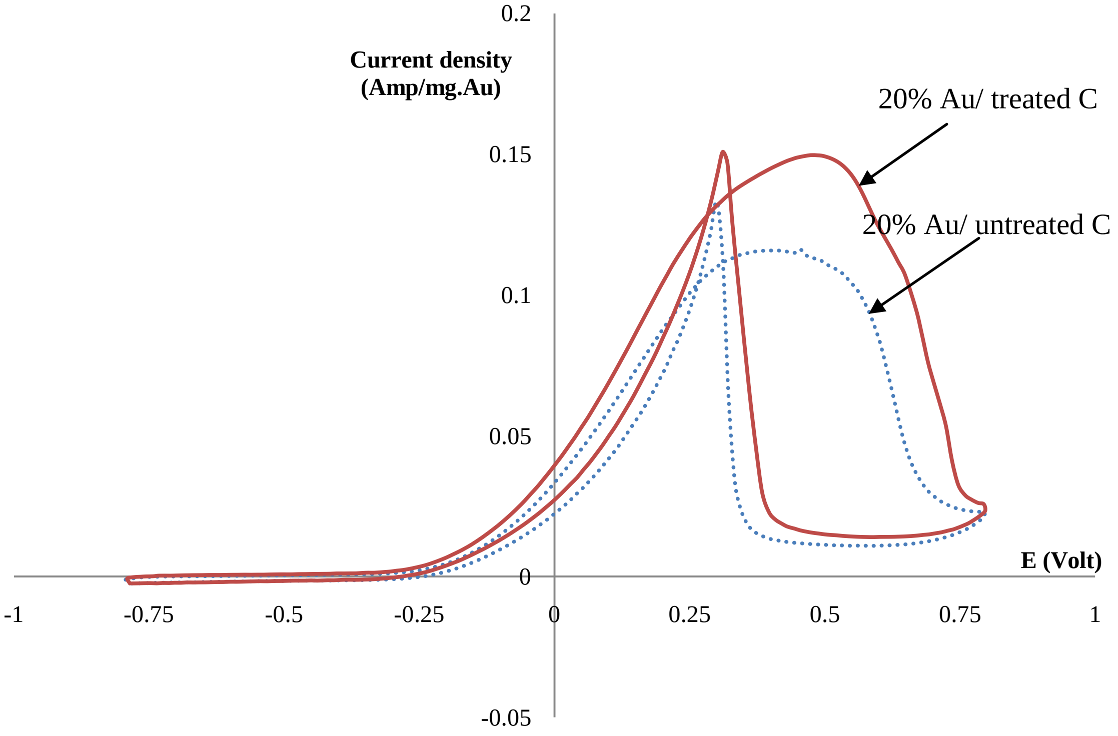


Figure 4.18 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M glycerol, scan rate 20 mVs^{-1} at 25 °C

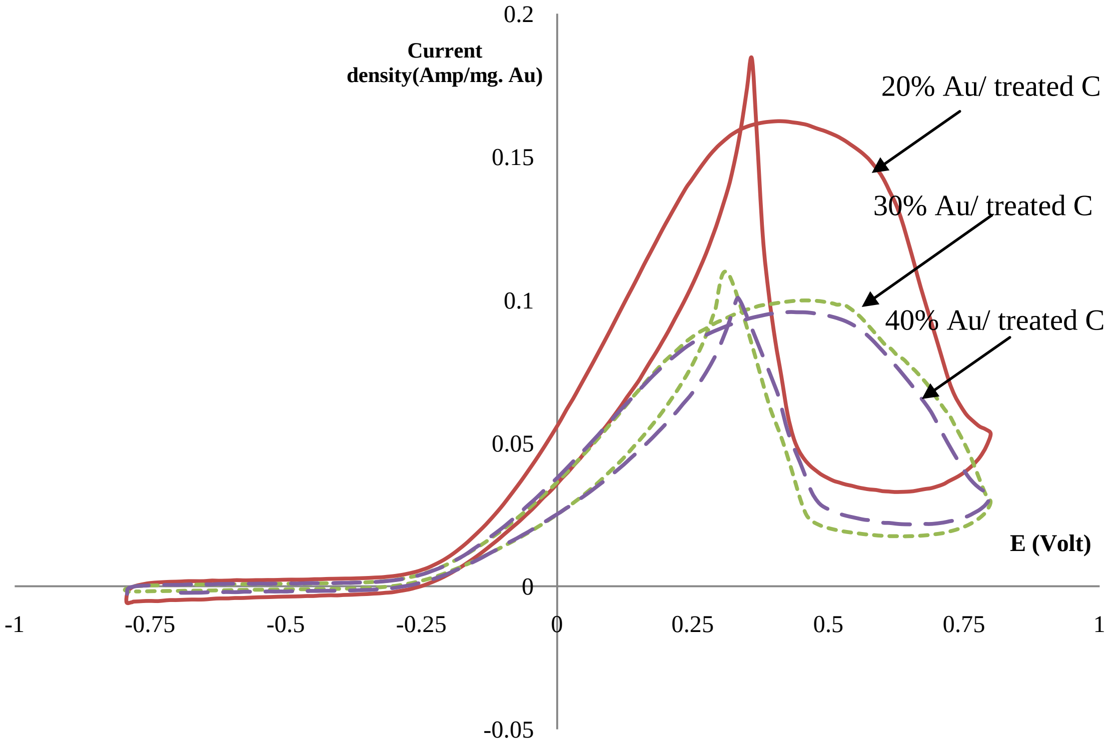


Figure 4.19 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M glycerol, scan rate 20 mVs^{-1} at 25 °C

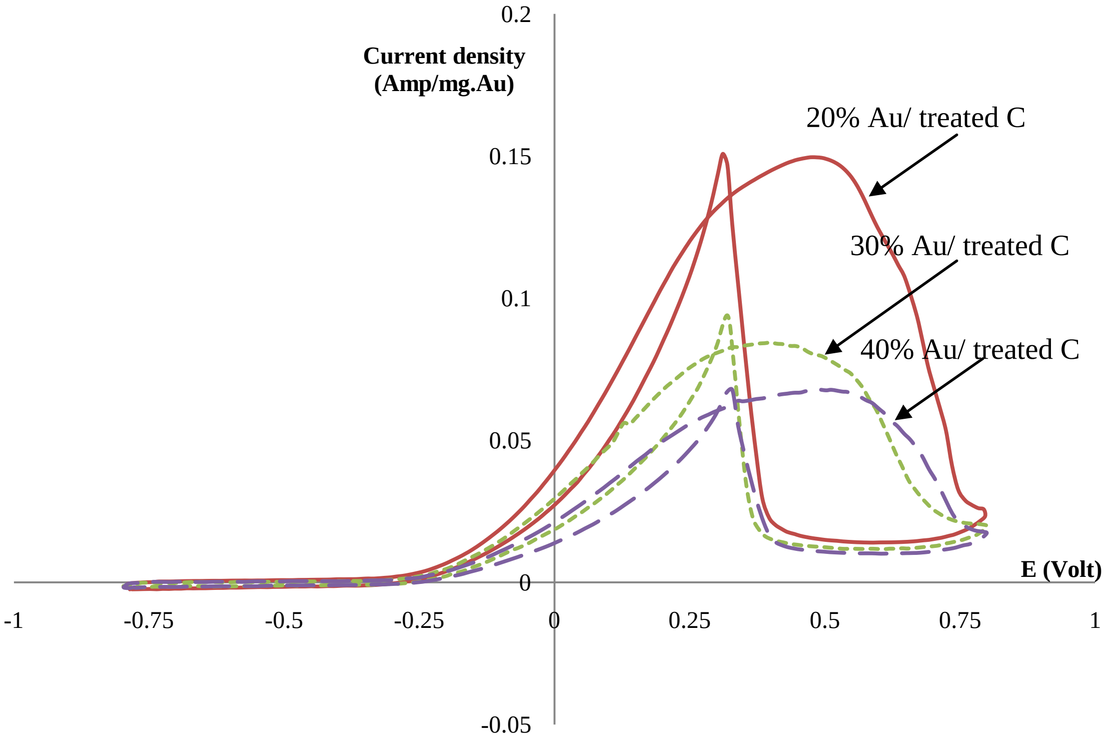


Figure 4.20 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M glycerol, scan rate 20 mVs^{-1} at 25 °C

Table 4.4 shows the current density of positive sweep oxidation in 0.1M KOH with 0.1M glycerol of different catalysts. In comparing between the catalysts prepared by the PVA and the citrate protection method, most of the catalysts by PVA method give higher current density than those by citrate protection method because of the size effect as previously discussed.

Table 4.4 Current density of positive sweep oxidation in 0.1M KOH with 0.1M glycerol

Catalyst	**Current Density Amp·mg Au^{-1}**
PVA method	
20% Au/ untreated C	0.0908
20% Au/ treated C	0.1625
30% Au/ treated C	0.1000
40% Au/ treated C	0.0958
Citrate method	
20% Au/ untreated C	0.1158
20% Au/ treated C	0.1496
30% Au/ treated C	0.0844
40% Au/ treated C	0.0678

4.3.3 Cyclic Voltammetry (CV) in 0.1M KOH with 0.1M ethylene glycol

Cyclic voltammograms of the ethylene glycol electrooxidation with all Au/C catalysts in a base solution are shown in Figure 4.21 to 4.24. Two oxidation peaks, forward and reverse oxidation peaks were observed which is similar to the glycerol cyclicvoltammograms. It can be seen that ethylene glycol elecrooxidation commences during the positive sweep at a potential of -0.25 V. This is the potential region before the surface oxide was formed on gold (see Figure 4.13 to 4.16), then ethylene glycol electrooxidation was inhibited by the surface oxide on the gold electrode from the potential of 0.4 V to 0.8 V. During the negative sweep, oxidation of ethylene glycol recurrented after the surface gold oxide has been reduced (see also Figures 4.31 to 4.16).

Figures 4.21 and 4.22 show cyclic voltammograms of the ethylene glycol electrooxidation by catalysts with treated and untreated carbon prepared by the PVA method and the citrate methods. From Figure 4.21, the peak current density obtained from ethylene glycol oxidation of all catalysts was very close and the effect of pretreatment of carbon support was less pronounced. It was also observed that with the same catalyst, the peak current densities obtained from ethylene glycol oxidation was less than those from glycerol oxidation. It was possibly that ethylene glycol was more difficult to oxidize than glycerol. Although the 20 wt% Au/ treated carbon had smaller Au particle size than that with untreated carbon, the peak current density obtained from both catalysts was about the same for the case of PVA method (see Figure 4.21) and slightly different for the case of citrate method (see Figure 4.22). For Figure 4.22, the result was in accord with glycerol oxidation.

Cyclic voltamograms of 20 wt%, 30 wt% and 40 wt% Au with treated carbon are shown in Figure 4.23 and 4.24. The reduction of peak current density with the increase in Au loading could be explained by the particle effect as described in section 4.3.2. Thus it can be ensured that influence of particle size, which was greater than the presence of gold oxide (AuOH) formed on gold electrode surface.

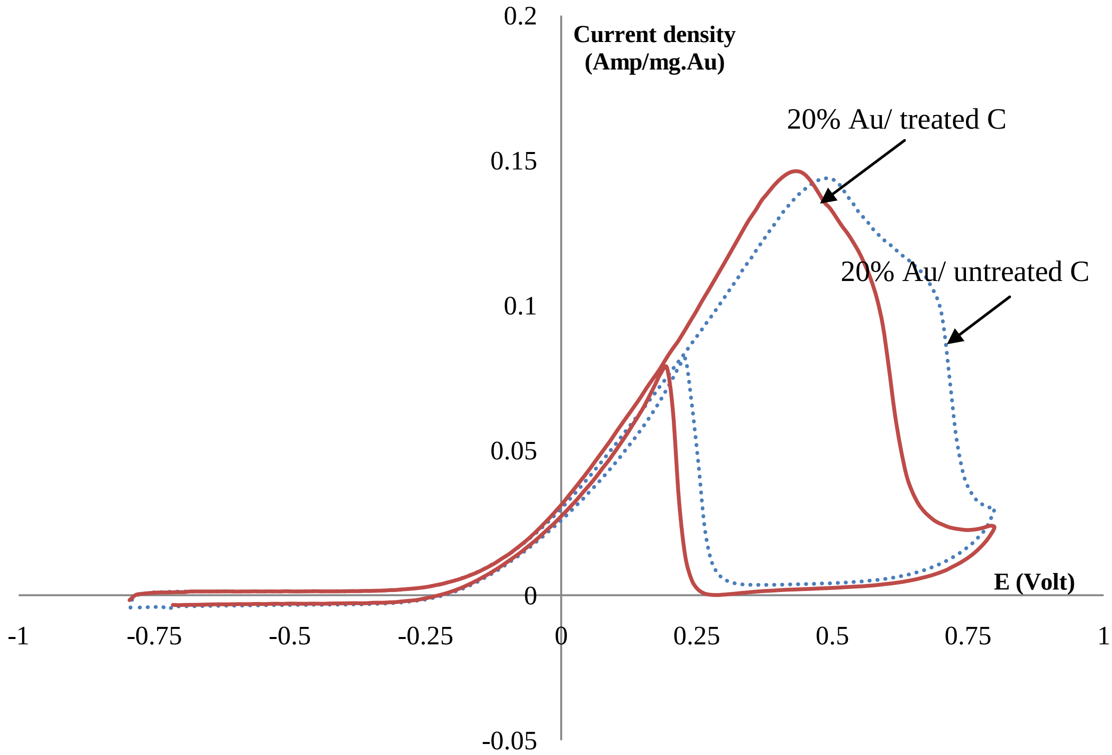


Figure 4.21 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M ethylene glycol, scan rate 20 mVs^{-1} at 25 °C

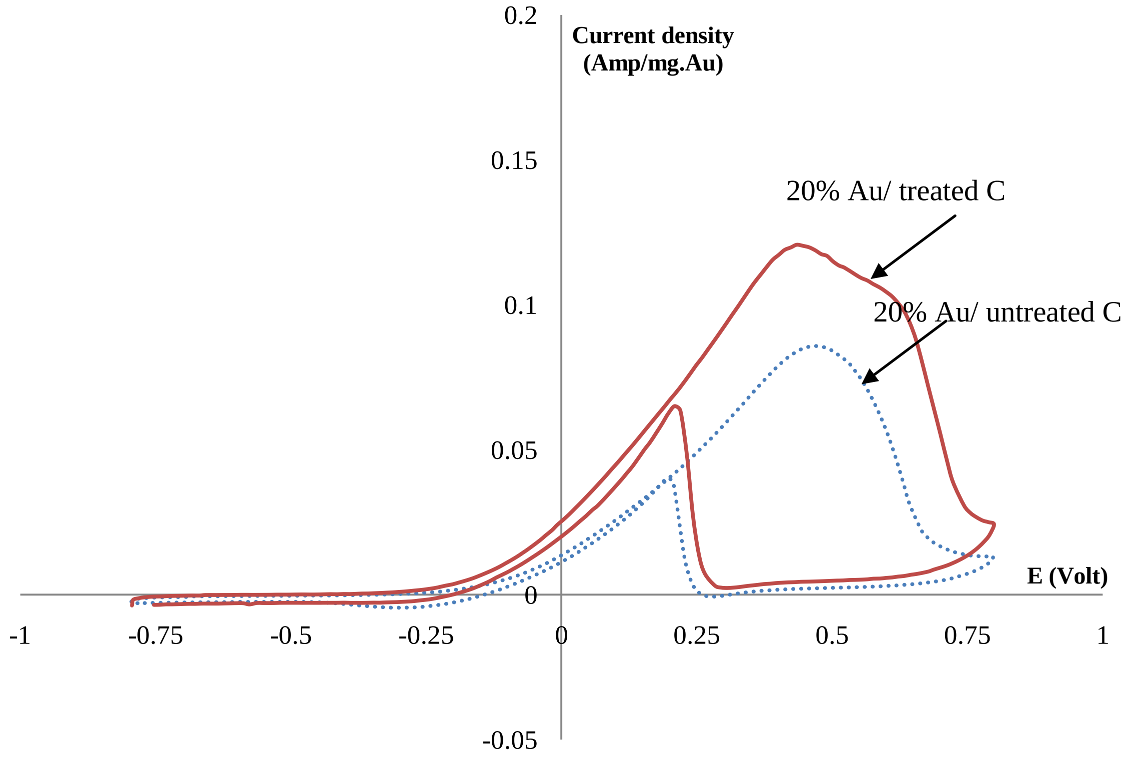


Figure 4.22 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M ethylene glycol, scan rate 20 mVs^{-1} at 25 °C

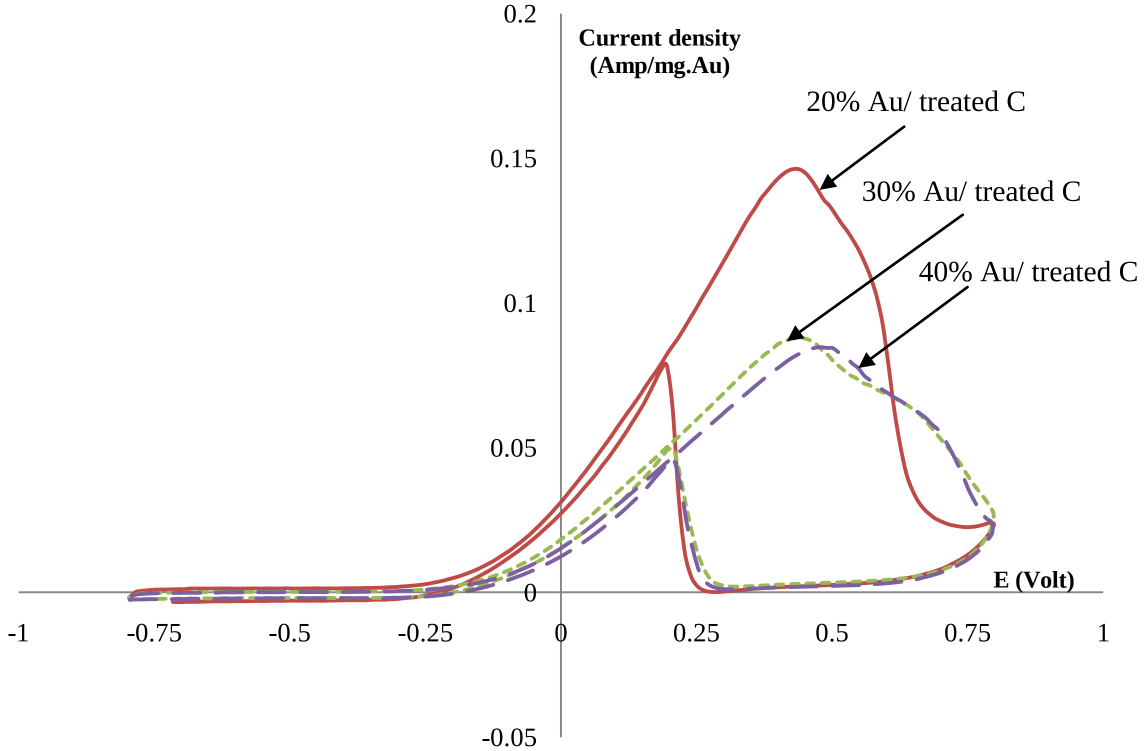


Figure 4.23 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M ethylene glycol, scan rate 20 mVs^{-1} at 25 °C

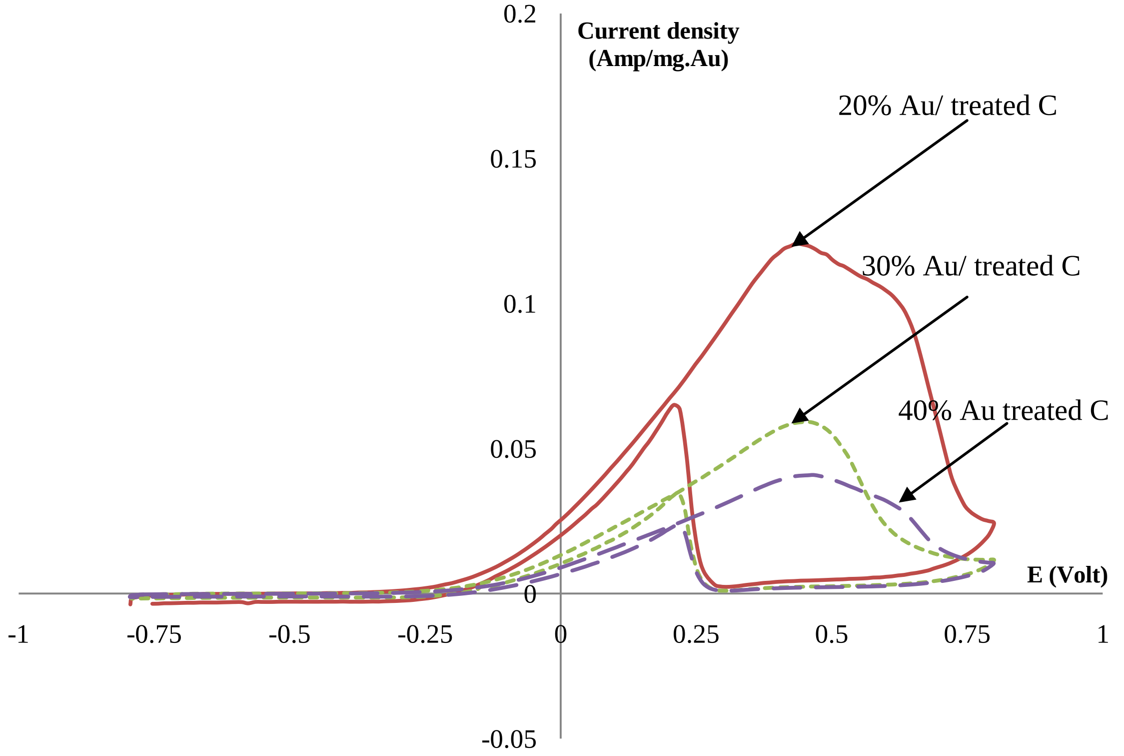


Figure 4.24 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M ethylene glycol, scan rate 20 mVs^{-1} at 25 °C

Table 4.5 shows the peak current density of the positive sweep oxidation in 0.1M KOH with 0.1M ethylene glycol of all catalysts. It can be seen that all catalysts prepared by the PVA method gave higher current density than these by citrate protection method. This tendency was also found in the case of glycerol oxidation.

Table 4.5 The peak current densities of the positive sweep oxidation in 0.1M KOH with 0.1M ethylene glycol for all prepared catalysts

Catalyst	**Current Density Amp·mg Au^{-1}**
PVA method	
20% Au/ untreated C	0.1439
20% Au/ treated C	0.1463
30% Au/ treated C	0.0879
40% Au/ treated C	0.0844
Citrate method	
20% Au/ untreated C	0.0858
20% Au/ treated C	0.1207
30% Au/ treated C	0.0592
40% Au/ treated C	0.0409

4.4 Chronoamperometry (CA)

Chronoamperometry (CA) was tested to ensure the results from CV. The catalyst was tested by holding the potential constant at 0.2 V and 0.4 V because alcohol could be significantly oxidized at those potentials. This technique was also used to determine the stability of catalyst by considering the decaying rate of each catalyst.

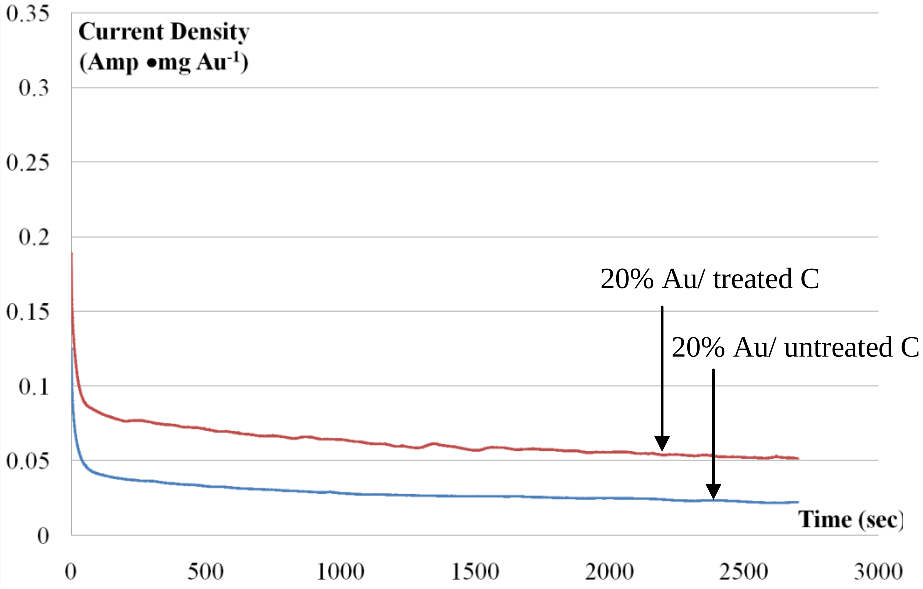
4.4.1 Chronoamperometry (CA) in 0.1M KOH with 0.1M glycerol

Chronoamperometry (CA) of Au/C catalysts prepared by PVA and citrate method in glycerol with alkaline solution at 0.2 V and 0.4 V were shown in Figure 4.25 to 4.28. After holding potential at 0.2 V and 0.4 V, the current generated from each catalyst drop rapidly at the initial, and then gradually decrease to approach a stable current density during 45 minutes of testing time.

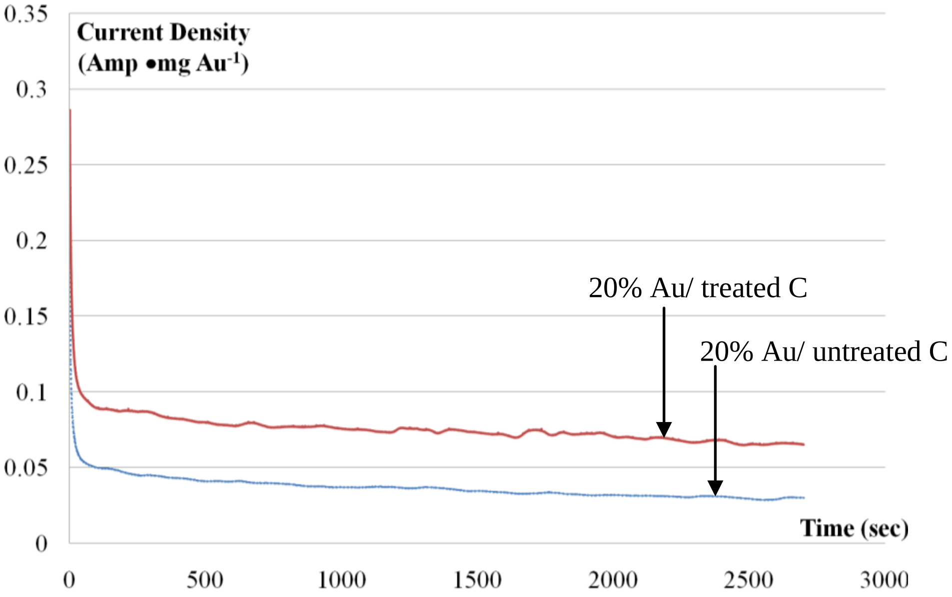
The average current from 10-45 minutes and a final stable current of these catalysts are concluded in Table 4.6. Furthermore, the slope of chronoamperometry can be used to determine the decaying rate of catalysts as shown in Table 4.7. In comparison to catalysts 20 wt% Au on treated carbon and untreated carbon of both catalyst preparation, the decaying rate of 20 wt% Au with treated carbon catalyst was lesser while the obtained current density was higher than that of 20 wt% Au on untreated carbon indicating that 20 wt% Au/ treated C was more tolerant to poison in glycerol oxidation. Therefore, it can be concluded that catalyst with treated carbon showed better performance than that with untreated carbon.

By increasing the amount of Au, the decaying rate was decreased. It can be explained that the catalyst with higher amount of Au was less active in glycerol oxidation producing less current density and less poisoning, thus decaying rate was low. Although 20 wt% Au catalysts with treated carbon had higher decaying rate, this catalyst generated current density higher than 30 wt% and 40 wt% Au catalysts with treated carbon in glycerol oxidation. Thus, 20 wt% Au catalyst with treated carbon was better than 30 wt% and 40 wt% Au of Au/C catalyst.

Furthermore, for considering the effect of catalyst preparation method, most of catalysts by prepared by PVA protection method provided higher current density and lower decaying rate thus; these confirm that Au/C catalysts prepared by PVA protection were more active than those by citrate protection method.



(a)



(b)

Figure 4.25 Chronoamperometric curves of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M glycerol at (a) 0.2 V (b) 0.4 V for 45 min

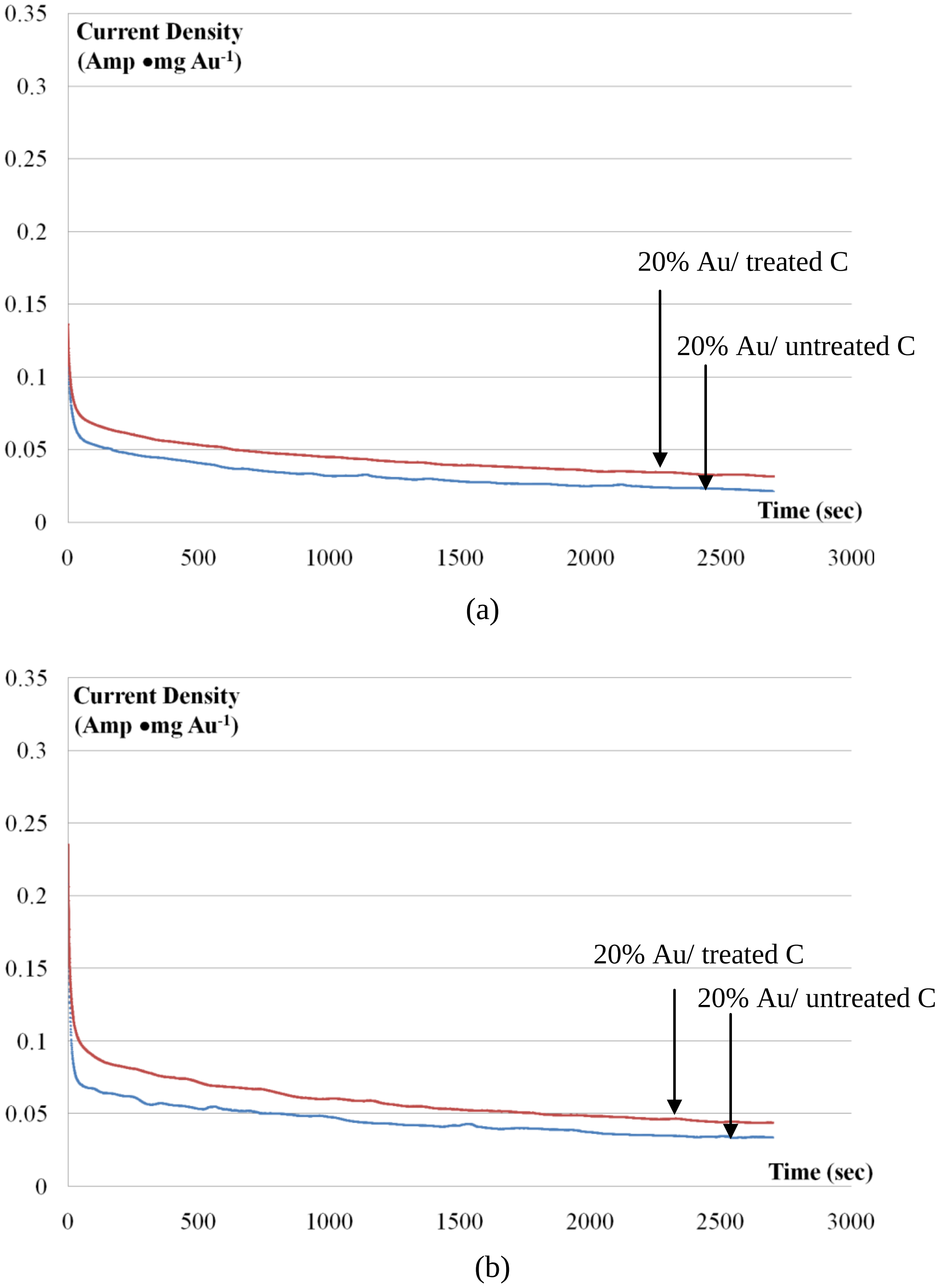
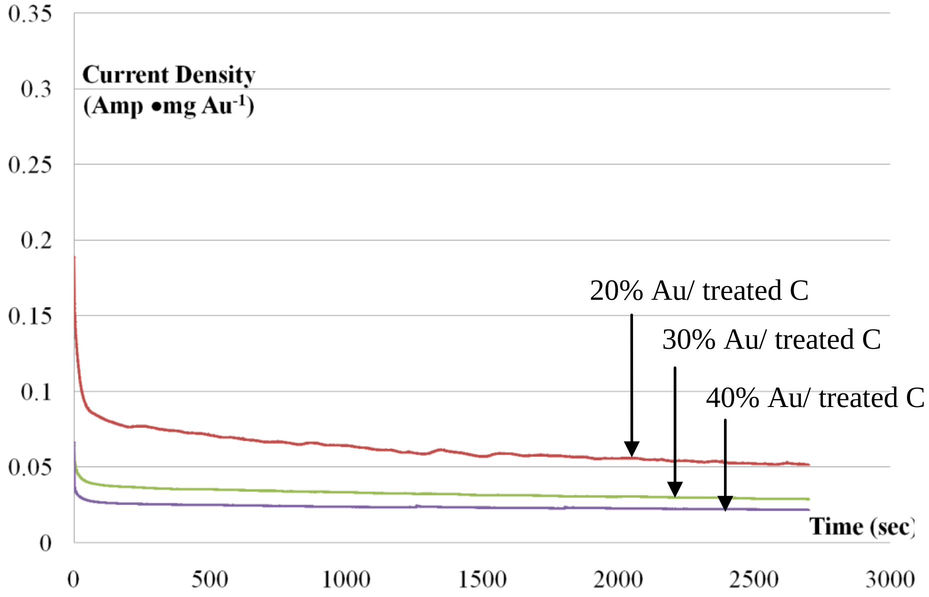
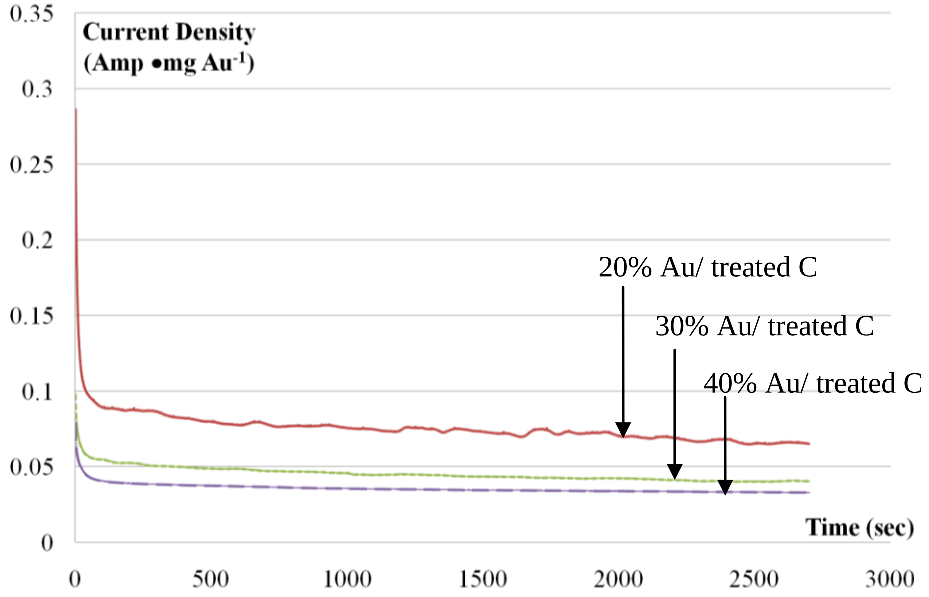


Figure 4.26 Chronoamperometric curves of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M glycerol at (a) 0.2 V (b) 0.4 V for 45 min

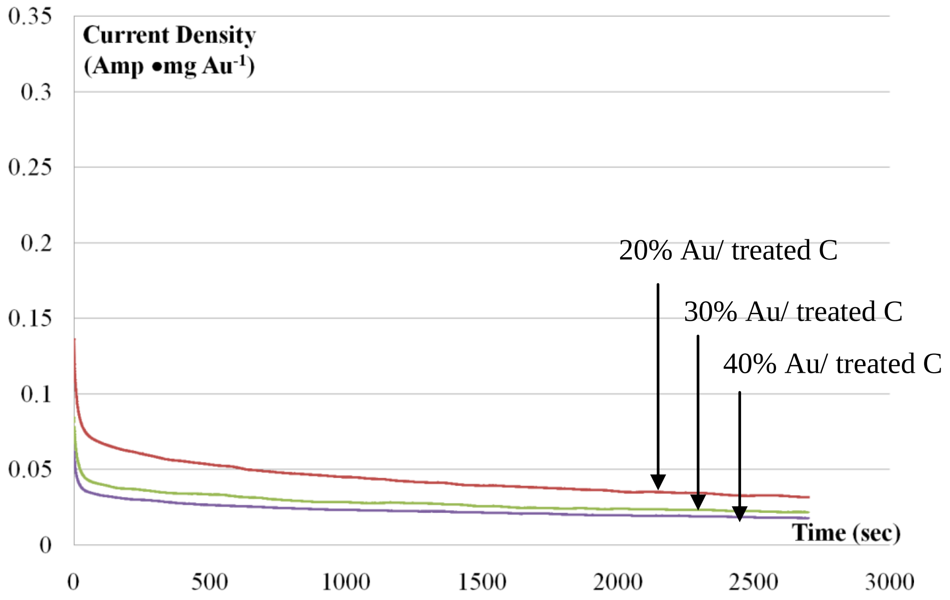


(a)

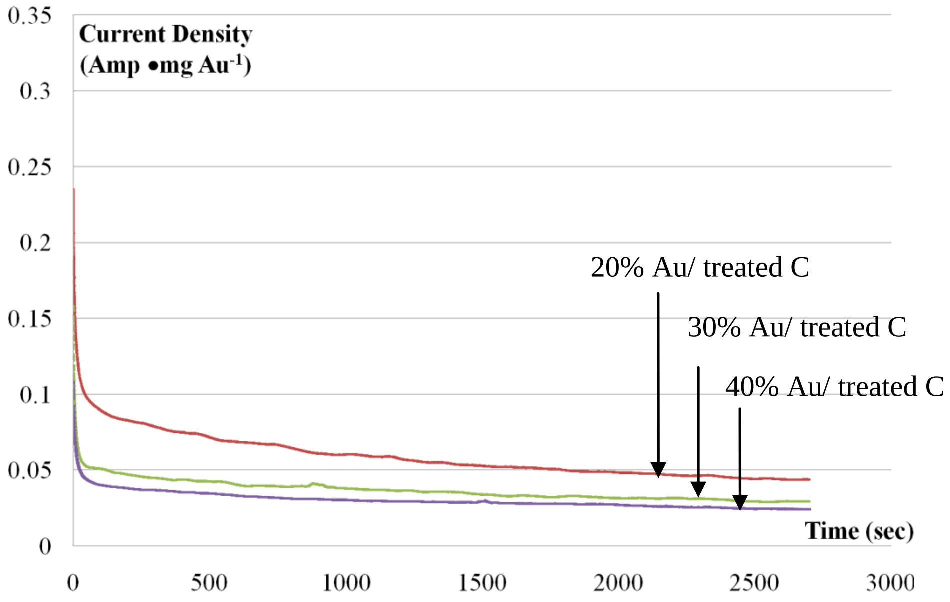


(b)

Figure 4.27 Chronoamperometric curves of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M glycerol at (a) 0.2 V (b) 0.4 V for 45 min



(a)



(b)

Figure 4.28 Chronoamperometric curves of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M glycerol at (a) 0.2 V (b) 0.4 V for 45 min

Table 4.6 Average current density and final stable current density from CA of Au/C catalysts in glycerol with alkaline solution by holding the potential constant at 0.2 V and 0.4 V

	At 0.2 V		At 0.4 V	
	Current density$_{ave}$ (Amp·mg Au^{-1})	Current density$_{final}$ (Amp·mg Au^{-1})	Current density$_{ave}$ (Amp·mg Au-^{1})	Current density$_{final}$ (Amp·mg Au^{-1})
PVA method				
20%Au/ untreated C	0.0250	0.0223	0.0331	0.0301
20%Au/ treated C	0.0566	0.0517	0.0711	0.0652
30%Au/ treated C	0.0308	0.0287	0.0424	0.0403
40%Au/ treated C	0.0228	0.0217	0.0340	0.0000
Citrate method				
20%Au/ untreated C	0.0265	0.0215	0.0387	0.0335
20%Au/ treated C	0.0372	0.0315	0.0503	0.0438
30%Au/ treated C	0.0246	0.0217	0.0328	0.0295
40%Au/ treated C	0.0202	0.0177	0.0272	0.0242

Table 4.7 Decaying rate of Au/C catalysts in glycerol with alkaline solution by holding the potential constant at 0.2 V and 0.4 V

	Decaying rate (% s^{-1})	
	at 0.2V	at 0.4V
PVA method		
20% Au / untreated C	0.0125	0.0125
20% Au / treated C	0.0108	0.0076
30% Au / treated C	0.0076	0.0075
40% Au / treated C	0.0050	0.0047
Citrate method		
20% Au / untreated C	0.0176	0.0163
20% Au / treated C	0.0161	0.0159
30% Au / treated C	0.0134	0.0129
40% Au / treated C	0.0131	0.0099

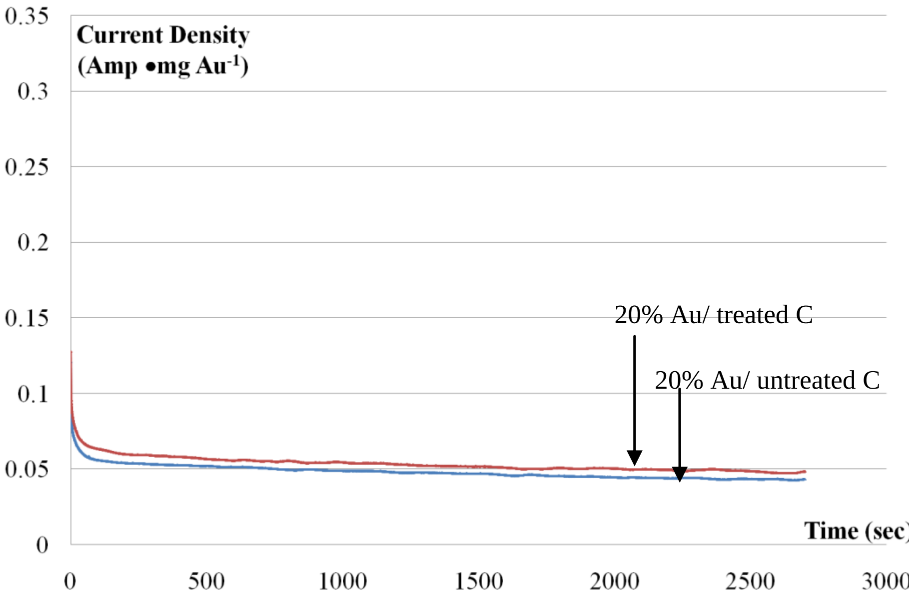
4.4.2 Chronoamperometry (CA) in 0.1M KOH with 0.1M ethylene glycol

Figure 4.29 to 4.32 show chronoamperometry (CA) of Au/C catalysts prepared by PVA and citrate method in ethylene glycol with alkaline solution at a potential of 0.2 V and 0.4 V. The current of catalysts drop rapidly at initial, and then decay slowly until 45 minutes.

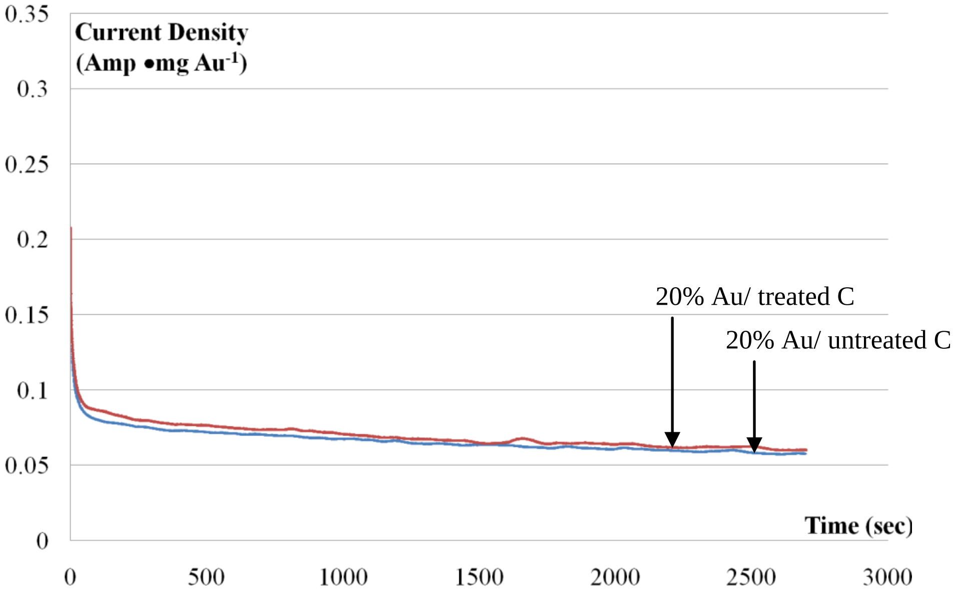
The average current density from 10 minutes to 45 minutes and final stable density current of these catalysts are summarized in Table 4.8 while the decaying rates of all catalysts are shown in Table 4.9. These results are in agreement with those in glycerol with alkaline solution. When the 20 wt% Au on treated carbon and untreated carbon catalysts of both catalyst preparation were compared, the decaying rate (from Table 4.9) of catalyst with treated carbon was smaller and current density (from Table 4.8) was also higher than that with untreated carbon especially at 0.4 V, thus it can be concluded that catalysts with treated carbon were better than those with untreated carbon in ethylene glycol oxidation.

Decaying rate was decreased as the amount of Au increased. The reason was already explained in section 4.4.1. However, although 20 wt% Au catalyst with treated carbon showed higher decaying rate, this catalysts still gave higher current density than 30 wt% and 40 wt% Au catalysts with treated carbon in ethylene glycol oxidation. Thus, 20 wt% Au catalysts with treated carbon were better than 30 wt% and 40 wt% Au catalysts.

For the effect of catalyst preparation method, most of catalysts prepared by PVA protection method have higher current density and lower decaying rate, suggesting that the Au/C catalyst prepared by PVA protection was more attractive than that prepared by citrate protection method.

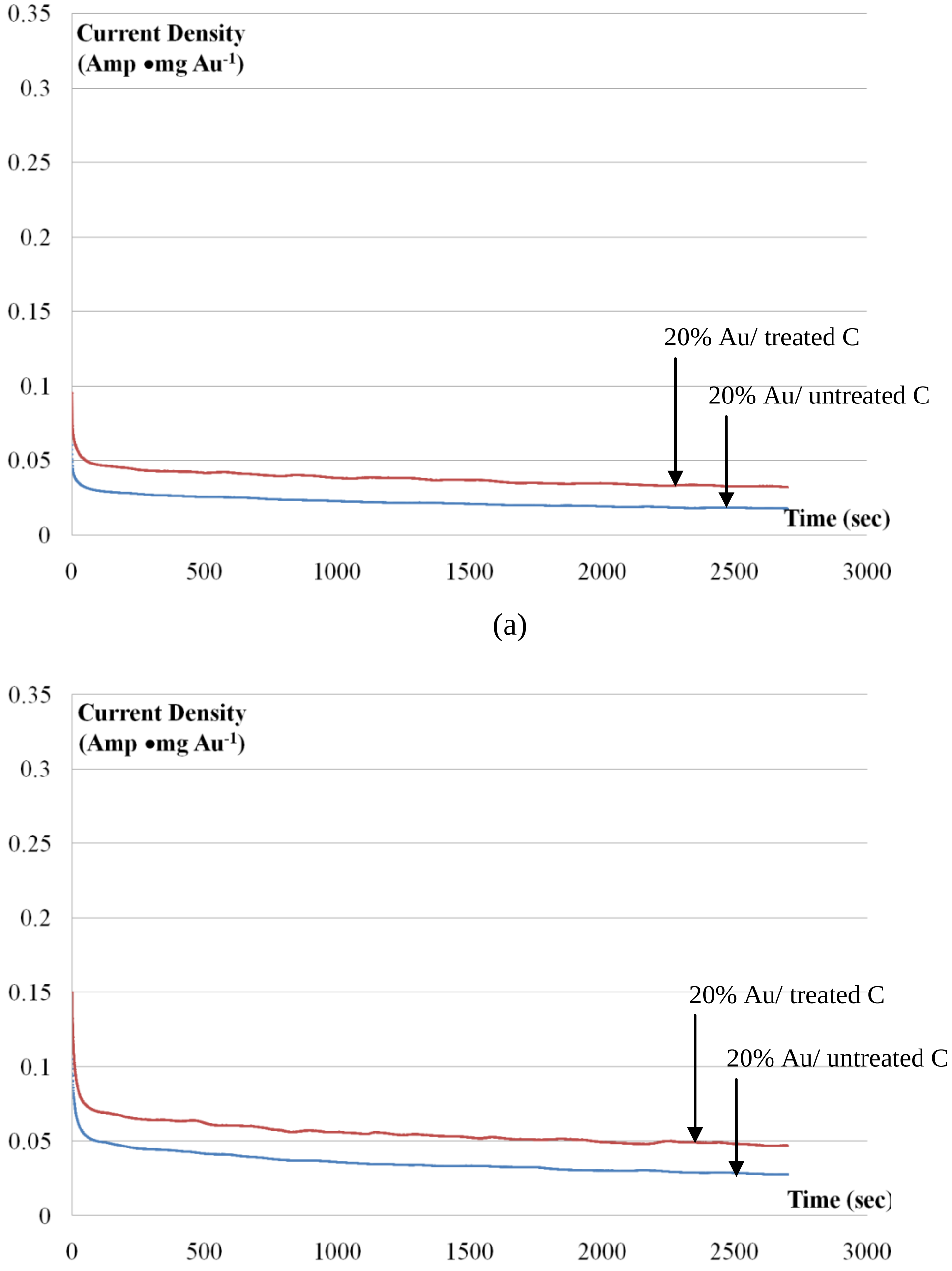


(a)



(b)

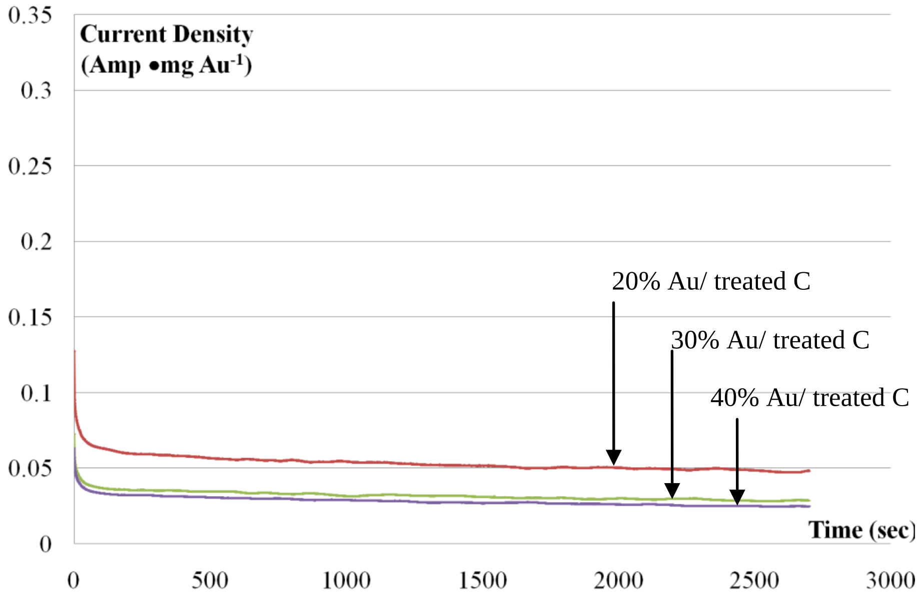
Figure 4.29 Chronoamperometric curves of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M ethylene glycol at (a) 0.2 V (b) 0.4 V for 45 min



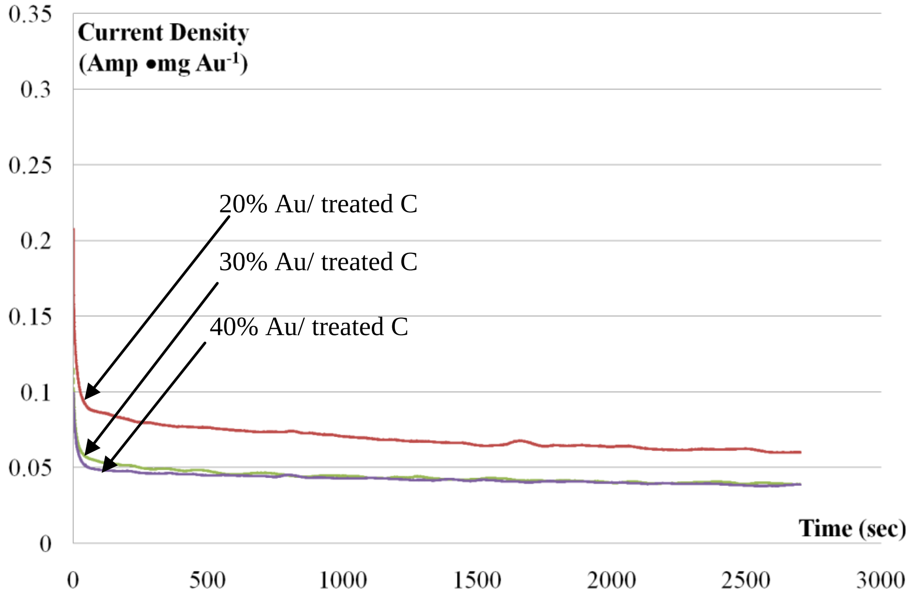
(a)

(b)

Figure 4.30 Chronoamperometric curves of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M ethylene glycol at (a) 0.2 V (b) 0.4 V for 45 min

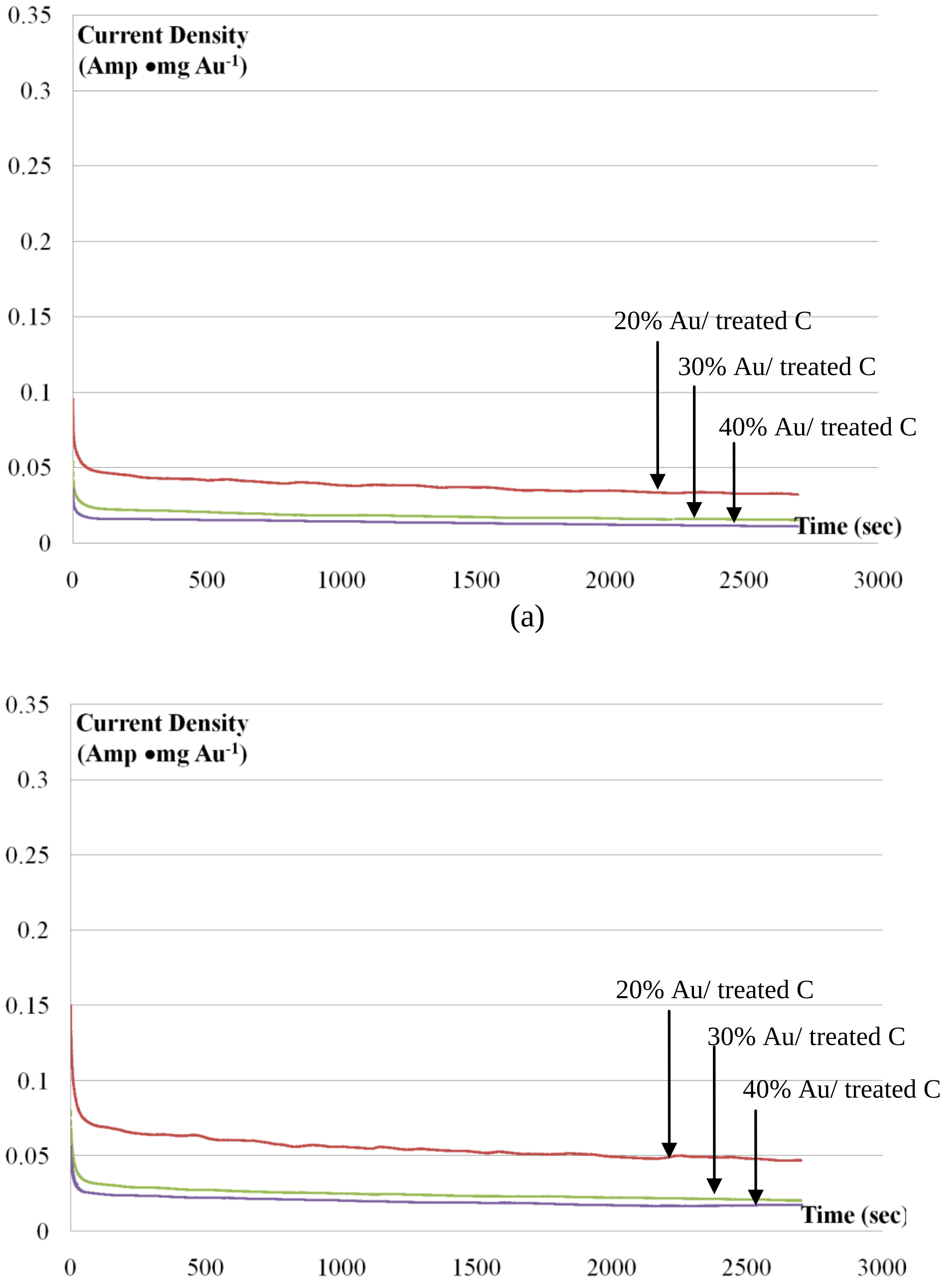


(a)



(b)

Figure 4.31 Chronoamperometric curves of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M ethylene glycol at (a) 0.2 V (b) 0.4 V for 45 min



(a)

(b)

Figure 4.32 Chronoamperometric curves of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M ethylene glycol at (a) 0.2 V (b) 0.4 V for 45 min

Table 4.8 Average current density and final stable current density from CA of Au/C catalysts in ethylene glycol with alkaline solution by holding the potential constant at 0.2 V and 0.4 V

	At 0.2 V		At 0.4 V	
	Current $\text{density}_{\text{ave}}$ (Amp·mg Au^{-1})	Current $\text{density}_{\text{final}}$ (Amp·mg Au^{-1})	Current $\text{density}_{\text{ave}}$ (Amp·mg Au-^{1})	Current $\text{density}_{\text{final}}$ (Amp·mg Au^{-1})
PVA method				
20%Au/ untreated C	0.0454	0.0432	0.0619	0.0577
20%Au/ treated C	0.0505	0.0483	0.0646	0.0602
30%Au/ treated C	0.0302	0.0287	0.0414	0.0391
40%Au/ treated C	0.0264	0.0246	0.0405	0.0388
Citrate method				
20%Au/ untreated C	0.0198	0.0178	0.0315	0.0278
20%Au/ treated C	0.0352	0.0322	0.0511	0.0471
30%Au/ treated C	0.0167	0.0153	0.0226	0.0204
40%Au/ treated C	0.0126	0.0110	0.0180	0.0174

Table 4.9 Decaying rate of Au/C catalysts in ethylene glycol with alkaline solution by holding the potential constant at 0.2 V and 0.4 V

	Decaying rate (% s^{-1})	
	at 0.2V	at 0.4V
PVA method		
20% Au / untreated C	0.0075	0.0085
20% Au / treated C	0.0066	0.0086
30% Au / treated C	0.0073	0.0069
40% Au / treated C	0.0085	0.0068
Citrate method		
20% Au / untreated C	0.0128	0.0129
20% Au / treated C	0.0098	0.0093
30% Au / treated C	0.0096	0.0098
40% Au / treated C	0.0122	0.0109