CHAPTER 2 THEORY AND LITERATURE REVIEW

2.1 Catalyst Preparation

The method of preparation strongly influences catalyst particle size. Furthermore, the size of gold particles is a very important parameter in obtaining highly active catalysts for many reactions. There are many methods of catalyst preparation which are described as follows [4].

2.1.1 Impregnation

This method is the simplest method which can be used with any support. The precursors often used are chloroauric acid ($HAuCl_4$) and gold chloride ($AuCl_3$). The oxide supports are used including silica, alumina, magnesia, titania and ferric oxide. This preparation method lead to large gold particles (10-35 nm) even for low gold loading (1-2 wt%), and poor catalyst activity.

2.1.2 Coprecipitation

Gold catalysts prepared by coprecipitation could be loaded on various oxides namely α–Fe_2O_3, NiO and Co_3O_4. This method leads to high gold dispersion and larger oxide surface area than that in the absence of gold. It is a single step method and easy to carry out. However, some of Au particles can be embedded in the bulk of support. One of the most widely studied materials made by this method is gold on iron oxide.

2.1.3 Deposition-precipitation

The method is commonly referred to deposition-precipitation, because metal hydroxide is precipitated on oxide support. It has been widely used for preparing oxide-supported gold catalysts having small particle size. A typical preparation method is as follows, adding the support to an aqueous solution of $HAuCl_4$ hydroxide or carbonate, then stirring under heating for 1 hour. Next the product is washed with water, dried and calcined in air.

2.1.4 Preparation of Gold Catalysts on Specific Supports: Gold on Carbon Supports

The previous methods are not suitable for obtaining small gold particles on activated carbon because of reducing nature of the carbon. That limits the deposition of gold in a dispersed state. Carbon is a very suitable support for gold in liquid-phase oxidation of organic compounds. Immobilization of gold colloid on carbon has been developed by using polyvinylalcohol (PVA) and polyvinylpyrrolidone (PVP) as stabilizers, particles 6-8 nm in size being obtained. Other stabilizers have proved effective. For use in liquid-phase reactions, removal of the stabilizer is unnecessary.

Thus, the stabilization of gold colloid on carbon by using stabilizers is suitable for preparing Au/C catalyst. The stabilization of colloid is described below.

2.2 Stabilization of Colloidal Metal Particles

Metal particles cannot stabilize in dispersing medium since small metal particles tends to agglomerate to form a bulk. Due to short interparticle distances, the particles would be attracted to each other by van der Waals forces leading to a coagulation of metal particles. The counteraction can be provided by the stabilizer [5]. There are two main classes of stabilizers, which are electrostatic stabilizer and steric stabilizer [6]. These modes of stabilization will be discussed in separate sections below.

2.2.1 Electrostatic stabilizer

The theory of electrostatic colloidal stabilization is described by using Derjaugin, Landau, Verwey, and Overbeek theory (DLVO theory) [6]. Colloidal stabilization is based on a balance of interparticle forces between repulsive Coulombic forces and attractive van der Waals forces. This theory is used for the system with weak or no interactions between colloid and solvent that so called lyophobic colloids-colloids.

The electrostatic stabilizers are the anions which are added to the solution as shown in Figure 2.1. Colloidal particle will be bound by anion. Then anions form a layer adjacent to the particle that leading to Columbic repulsion between other particles, now anionically charged particles. This Columbic repulsion will prevent particle agglomeration. Cations are also present to provide charge balance and complete the electronic multilayer while monoanions such as halides ion sometimes are closet. The examples of electrostatic stabilizer are trisodium citrate, tetrakishydroxypropylphosphonium chloride (THPC) and tetrahydrofuran (THF) etc.

The limitations of DLVO theory are that it is not designed to account for counterions with multiple charges and it is not appear to work well in more concentrated system where dispersion force may dominate the electrostatic forces.

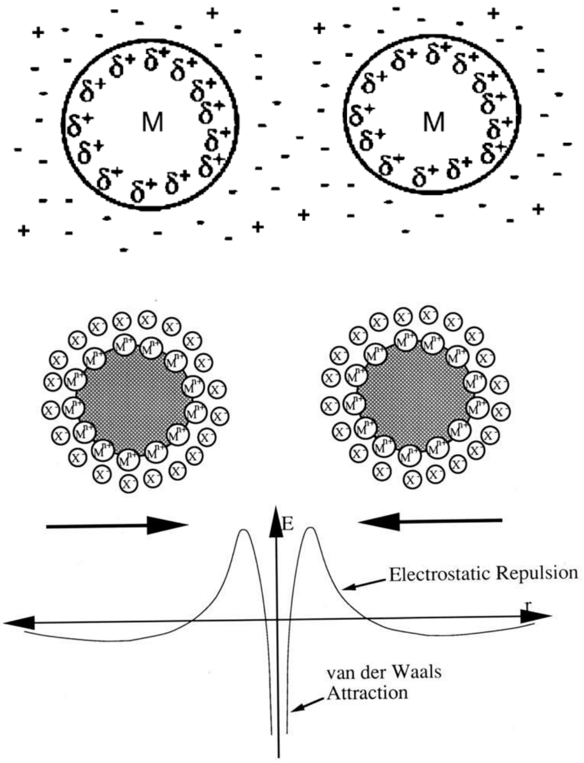


Figure 2.1 Electrostatic stabilization of metal colloid particles [5-6]

2.2.2 Steric stabilizer

There are many types of steric stabilizer namely polymer, siloxane polymers, dendrimers, microgels, alkanethiol (and other) surfactants, resorcinarenes, amines and phosphines and branched polymer [6]. For this work, the polymer was used as the steric stabilizer, thus only polymer type will be described below.

Polymers are mostly used as the steric stabilization. The molecules of polymer are adsorbed by the colloidal particles. The polymers stabilize not only at least in part by ligation of colloid surface, but also by occupying space around the colloid. These lead to discourage the contact between the colloids to prevent the agglomeration.

One model of polymer stabilization is written as if one polymer chain stabilizes one nanocluster as shown in Figure 2.2 (a) while Talylor dispersion indicates that one polymer chain can attach to multiple nanoclusters as displayed in Figrue 2.2 (b).

Colloids or nanocluster of transition metal have been prepared by a variety of polymer such as polyvinylpyrrolidone and polyvinyl alcohol. PVA polymers in nanocluster system have the potential to serve as both the reductant of the organometallic complex and the nanocluster stabilizer.

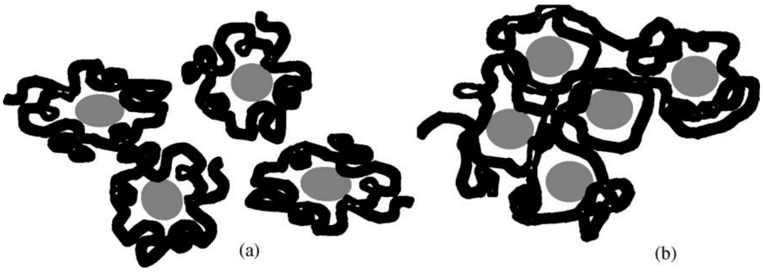


Figure 2.2 Two possible polymer stabilizer (a) colloid with individual polymer chains (b) multiple colloids with single polymer chain [6]

2.3 Catalyst Characterization

2.3.1 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectrometry (AAS) is a spectroanalytical procedure for the qualitative and quantitative determination of chemical elements. This method applies the absorption of light by free atoms in the gaseous state. This technique is used for determining the concentration of a particular element in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or in solid samples. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption.

2.3.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a well known technique for imaging solid materials at atomic resolution. TEMs are a major analysis method in a range of scientific fields, in both physical and biological sciences. This technique uses a beam of electrons. It is transmitted through a thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen. TEMs are capable of imaging at a significantly higher resolution than light microscopes because of the small de Broglie wavelength of electrons. For this work, TEM technique is used to determine particle size and size distribution of gold particles deposited on carbon support.

2.4 Electrooxidation of catalyst in alcohol

2.4.1 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is the most widely used to perform electrochemical technique. CV has been used for studying such as reaction analysis on an electrode surface and determining the electrochemical surface area (ESA) [7]. Generally, principle of the CV measurement is that the electrode undergoes a steady voltage potential sweep from low potential to high potential and resulting current generated at the electrode is measured. Normally, reference (RE), counter (CE) and working electrode (WE) are used in CV analysis. A typical CV of platinum electrode in an alkaline solution is shown in Figure 2.3.

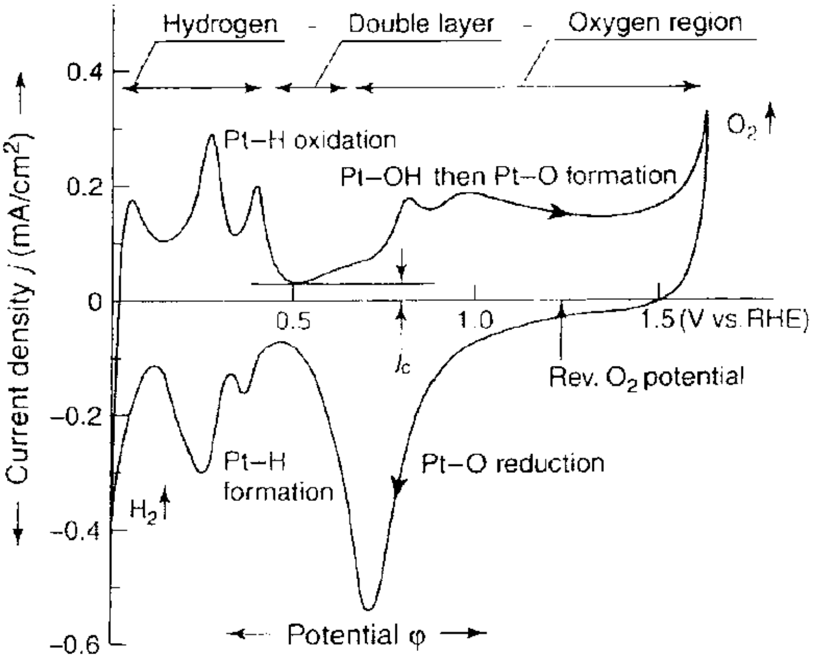


Figure 2.3 A typical CV of platinum electrode in alkaline solution [7]

At a low potential, it is the hydrogen oxidation region it contains several peaks which are the reaction flowers:

In alkaline solution:

$$\text{Pt—H} + OH^- \rightarrow \text{Pt} + H_2O + e^- \qquad (2.1)$$

While in acid solution:

$$\text{Pt—H} + H_2O \rightarrow \text{Pt} + H_3O^+ + e^- \qquad (2.2)$$

At higher potential, there is a double layer charging with no significant electrochemical reactions. Above ~800 mV the platinum oxidation takes place as the following reaction;

In alkaline solution:

$$\mathrm{Pt + OH^- \rightarrow Pt\text{—}OH + e^-} \qquad (2.3)$$

$$\mathrm{Pt\text{—}OH + OH^- \rightarrow Pt\text{—}O + H_2O + e^-} \qquad (2.4)$$

In acid solution:

$$\mathrm{Pt + H_2O \rightarrow Pt\text{—}OH + e^- + H^+} \qquad (2.5)$$

$$\mathrm{Pt\text{—}OH + H_2O \rightarrow Pt\text{—}O + H_3O^+ + e^-} \qquad (2.6)$$

At very high potential, the oxygen evolution reaction occurs as follows;

In alkaline solution:

$$\mathrm{4OH^- \rightarrow O_2 + 2H_2O + 4e^-} \qquad (2.7)$$

In acid solution:

$$\mathrm{2H_2O \rightarrow O_2 + 4H^- + 4e^-} \qquad (2.8)$$

After that the potential is then swept backward. The oxygen and Pt—O reduction reactions occur via the reversed reaction of (2.4) and (2.3) for alkaline solution and (2.6) and (2.5) for acid solution, respectively.

At the lower potential, hydrogen starts adsorbing on platinum via the following reactions;

In alkaline solution:

$$\mathrm{Pt + H_2O + e^- \rightarrow Pt\text{—}H + OH^-} \qquad (2.9)$$

In acid solution:

$$\mathrm{Pt + H_3O^+ + e^- \rightarrow Pt\text{—}H + H_2O} \qquad (2.10)$$

At very low potential, hydrogen evolution observed:

In alkaline solution:

$$\mathrm{2H_2O + 2e^- \rightarrow 2OH^- + H_2} \qquad (2.11)$$

In acid solution:

$$\mathrm{2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2} \qquad (2.12)$$

These are the reactions of platinum electrode in CV. The main reactions in CV are the platinum oxidation (reaction of (2.3)-(2.4) or (2.5)-(2.6)) on the positive sweep, and the oxygen and Pt—O reduction (reversed reaction of (2.4)-(2.3) or (2.6)-(2.5)) on the negative sweep. For the reaction of gold in CV, it will be described in literature review.

Additionally, Electrochemical Surface area (ESA) can be determined by CV technique. ESA is used to describe the efficiency of catalyst on electrode. To calculate the ESA, the area of current versus time plot during the reduction peak in CV is used to determine the total charge per superficial electrode area. Then the value of charge is divided by the total catalyst loading and a proportionality constant for a given catalyst to obtain the ESA value.

$$\mathrm{ESA}=\frac{\int I(t)dt}{S\cdot C} \quad (\mathrm{m^2/g_{catalst}}) \qquad (2.13)$$

where S is a proportionality constant that used to convert the charge per area to effective catalyst active area, i.e., 386 µC/cm^2 for gold and 210 µC/cm^2 for platinum. C is the loading of the catalyst in grams.

2.4.2 Chronoamperometry (CA)

Chronoamperometry is a technique in which the electrode is held at constant potentials for a long time. For CA, the average current over the time can be determined while for CV, current is considered at individual time. Additionally, it can be used to determine the stability of catalyst on electrode on the length of time by calculating the slope of current versus time plot.

2.5 Literature review

J. Thepkaew, et al. [8] studied the effect of carbon support pretreatment on PtSn/C performance. Pretreatment of carbon support comprises of acid (HNO_3) and thermal treatments. The results show that after pretreatment, the specific surface area of carbon increases from 193 m^2/g to 202 m^2/g and 265 m^2/g for chemical treatment and thermal treatment, respetively. In addition, thermal treatment can generate more micro pores leading to a reduction of average pore radius. The reduction is attributed to the removal of inorganic matter and less stable oxygen complexes on the support surface at high temperature.

L. Prati, et al. 1999 [9] found that Au/C catalysts are a good catalyst for liquid-phase oxidation of ethane-1,2-diol (ethylene glycol). This catalyst resist to poisoning. They prepared the Au/C catalysts by deposition-precipitation and supported metallic sol methods. They found that deposition-precipitation method not suitable for Au/C preparation because it gives large aggregate of gold. For the supported metallic sol method, they used PVA as the protective agent. They prepared catalyst by using $HAuCl_4$ as the precursor, fixing the PVA/Au ratio at 0.62 (wt/wt) and $NaBH_4$/Au at 4 (mol/mol) to ensure the complete reduction of Au(III) to Au(0). The results show that gold particles well disperse on carbon support and high catalyst activity in liquid-phase oxidation of ethane-1,2-diol. They also found that the particles size about 7-8 nm gives the maximum activity, with larger and smaller particle sizes being less active and less selective.

F. Porta, et al. [10] studied about selective oxidation of glycerol to sodium glycerate with gold-on-carbon catalyst. They used different catalyst preparation methods (incipient wetness, impregnation, sol immobilization) and different supports (active carbon, graphite, and carbon black). The mean Au particle dimension was determined by using XRPD and HRTEM and the surface exposition for each catalyst was obtained from XPS. The catalysts prepared via sol immobilization (PVA, THPC), typically constituted by 4-5 nm of well-dispersed gold nanoparticles show the highest activity. These catalysts have small particle size and are characterized by good surface exposition, with corresponding higher activity.

DiScipio, et al. [11] prepared the colloidal gold particles by using PVA as the protective agent. They studied the effect of reducing agent type including sodium borohydride and sodium cyanoborohydride on Au particle size. They found that different reducing agent could generate different Au particle sizes. The results showed that the particle size of gold reduced by sodium borohydride could be either small size (20 A°) or large size (300 A°) depending on the initial concentration of tetrachloroauric acid. By using cyanoborohydride as the reducing agent, the medium size of gold particle (100 A°) was obtained. Additionally, they found that the temperature is not a major factor for producing gold particles of different size.

F. Porta, et al. [12] conducted experiment to synthesize sol by using different types of auric precursors ($AuCl_3$, $NaAuCl_4$ and $HAuCl_4$), the reducing agents ($H_2C_2O_4$, $SnCl_2$ and $NaBH_4$) and the stabilizing compounds (PVA and PDDA). Then the prepared catalysts were tested in the liquid-phase oxidation of ethylene glycol to glycolate. Firstly, they found that the type of gold precursors was not affect the final gold catalyst activity. The effect of reducing agent on the size and size distribution of particles was very high. $H_2C_2O_4$ and $SnCl_2$ were not useful for generating good catalysts for liquid-phase oxidation. The increasing molar ratio of the reducing agent ($NaBH_4$) to Au results in decreasing the Au particle size. Finally, the amount of the protective agent is also important for the immobilization on carbon The results show that a lower amount of protective agent produced more active catalysts which contradicts with the results of L. Pratt 1999 [9]. The increasing in catalytic activity appeared to be very high because of a decrease in mean size diameter and a lack of drawback of shielding the metal particle by the protective agent (PDDA).

S. Biella, et al. [13] found that the controlling factor of gold particle size on carbon support was not the total amount of $NaBH_4$ but the kinetics of metal sol formation which is depend on the $NaBH_4$ addition: in one step or in portions. The results show that the Au/C catalyst by dropwise $NaBH_4$ addition gives the highest activity although the particles size is the same with others. Thus they also concluded that the catalyst activity was not ruled only by the dimension and the exposure of gold.

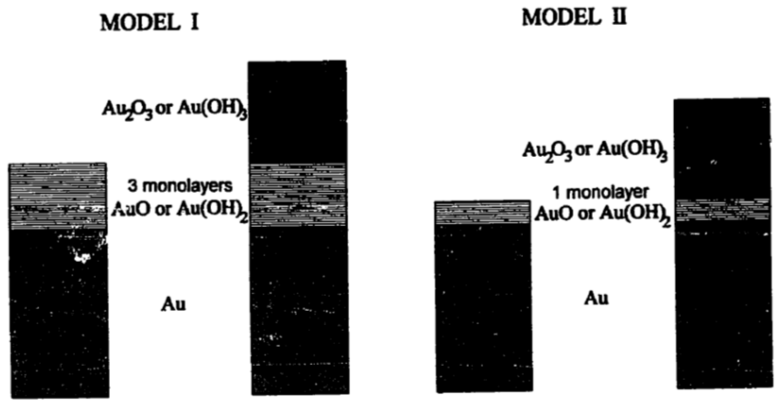
W. Chen, et al. [14] prepared the Au/C catalyst by PVA protection method and pre-precipitation method. Then, the electrochemical activities of these catalysts were measured. The results show that the catalyst prepared with the PVA protection method gives the current density of oxygen reduction more than that prepared with the pre-precipitation method, demonstrating the higher electrocatalytic activity of catalyst obtained from the PVA protection method. This is due to the small average size and low relative crystallinity of the Au particles in the Au/C catalyst prepared by the PVA protection method.

T. Inasaki, et al. [1] investigated the influence of cluster size of Au catalysts on the kinetics of oxygen reduction reaction (ORR) in acidic medium. They prepared gold nanoparticles by using triphenylphosphine-protected gold sol and citrate-protected gold sol. For the citrate protected gold sol, two different types of reducing agents, citrate itself and $NaBH_4$ were used with controlled solution temperature at 70°C and 0°C, respectively. Then the catalyst was characterized by TEM and measured the electrochemical activity by using CV technique in acid solution. It was found that the Au particle size and its size distribution depend on the catalyst preparation method. The triphynylphosphine-protected gold sol provided the smallest Au particle with nearly monodispersed size distribution, while the citrate-protected gold sol gives larger Au particles and broader size distribution. The particle size of the Au/C catalyst reduced by $NaBH_4$ was smaller than that reduced with citrate but both have same size distribution. For Au/C catalysts with smaller Au particle sizes, the cathodic peaks at 0.94 V, corresponding to Au oxide reduction reaction were larger than those for the Au/C catalysts with larger Au particle size, because of higher surface area of the smaller particles. In addition, the activity of the 2-step 4-electron reduction was higher when the size of Au particles was less than 3 nm.

N. Dimitratos, et al [2] studied about the effect of catalyst preparation method (deposition-precipitation versus sol immobilization) and reduction method (calcinations versus chemical reduction) on Au/TiO_2 catalysts for the liquid phase oxidation of glycerol. It was found that not only the choice of the reduction method but also the use of protective agents (PVA, THPC) for stabilization of the gold colloid could affect the activity of the prepared catalyst. It was found that the catalytic activity is shown to be dependent not only on the choice of the reduction method but also on the use of protective agent (PVA, THPC) for the stabilization of the gold colloids. When a low temperature chemical reduction was employed on a Au/TiO_2 sample synthesized by the deposition-precipitation method, the highest activity was obtained. The use of a higher pre-treatment temperature or a protective agent resulted in a lower activity.

G. Tremiliosi-Filho, et al. [15] proposes the possible model of gold oxide formation on electrode. They explained that thick oxide film which occurred by potentiostatic polarization of Au electrode comprise four oxide states namely OC1, OC2, OC3 and OC4. The OC1 state is the first feature in the oxide reduction profile and it slowly grows to a limiting thickness while the OC2, OC3 and OC4 states rapidly grow without the limitation thickness. OC1 state corresponds to development of quasi-2D state and very initial growth of the OC2 state, and the oxide growth is slow. Further growth of OC2 and formation of OC3 and OC4 state is significantly faster as shown in Figure 2.4. They defined the inner layer as α and outer layer as β. The α film corresponds to the

OC1 state while the β film corresponds to OC2, OC3 and OC4 state. The OC1 state (α film) reaches a limiting thickness of 3 monolayers of AuO or $Au(OH)_2$ in acid solution and 1 monolayer of AuO or $Au(OH)_2$ in base solution. For OC2, OC3 and OC4 states (β film) occur at outer oxide film having the Au_2O_3 or $Au(OH)_3$ without the thickness limit.



(a) (b)

Figure 2.4 (a) Model I: model of thin and thick Au oxide films formation in acid solution, (b) Model II: model of thin and thick Au oxide film formation in base solution [15]

L D Burke, et al. [16] explain the reactions of gold oxide formation/reduction which occur in electrode by CV technique. Commonly, feature of monolayer oxide formation/reduction is hysteresis. Hysteresis is the difference of potential range for monolayer oxide formation in the positive sweep as compared with that for monolayer oxide reduction in the negative sweep. Hysteresis in the monolayer oxide formation is attributed to gradual changes in the nature of the oxide film. The dipolar ($Au^{\delta+}$—$OH^{\delta-}$) species are produced which at appreciable coverage, repel one another. Repulsion energy raises the energy required to generate additional dipoles; thus there is an increase in potential with increasing coverage. These lead to an extended of plateau rather than a sharp peak in positive sweep in Figure 2.5. Then, rotation of some of the surface dipoles (referred to as place-exchange) occurs, and then relieves much of the lateral repulsion or stress in the surface layer as shown in Figure 2.6. Therefore no electrostatic cathodic peak is observed (see Figure 2.5).

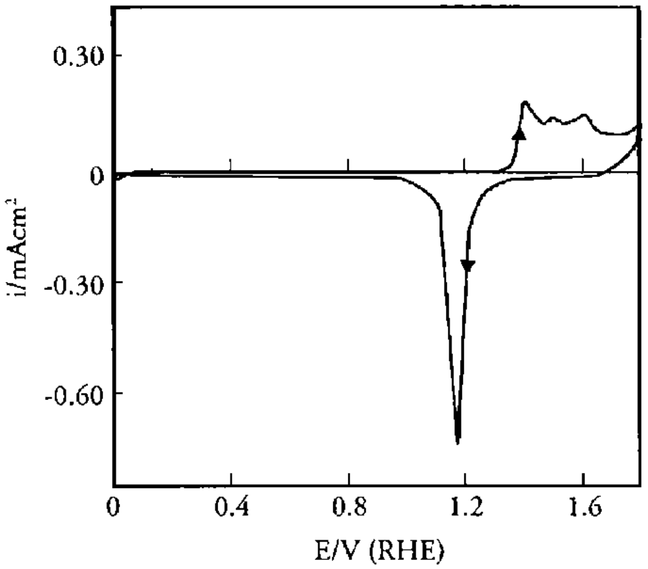


Figure 2.5 Typical CV for a poly crystalline gold disc electrode in acid solution [16]

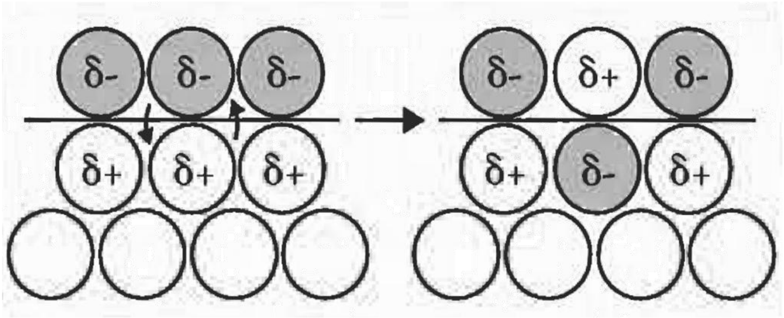


Figure 2.6 Place-exchange reaction involved in a monolayer oxide formation, unshaded circle defined as the metal atoms and shaded circles defined as adsorbed oxygen species [16]

Additionally they explain that there is another factor, related to change in the activity of surface metal atoms, that may contribute to the hysteresis effect. There are three state of gold atom including (i) bulk lattice atoms (Au^0) which have little relevance to the reaction at the surface, (ii) regular surface atoms (Au*) which are more active than those in the bulk atom and (iii) displaced surface atoms (Au**) which are in a state of higher activity as these are generated initially in a state of unusually low lattice coordination number on reduction of the partially place-exchanged surface oxide. The (iii) state of gold atoms is assumed to rapid change to the (ii) state.

According to the hysteresis, the Figure 2.6 can be used to describe in terms of the reaction. When considered the reaction in Figure 2.7, it can be seen that these reaction corresponds to the reaction of platinum oxidation and reduction in acid solution from reaction 2.5 and 2.6.

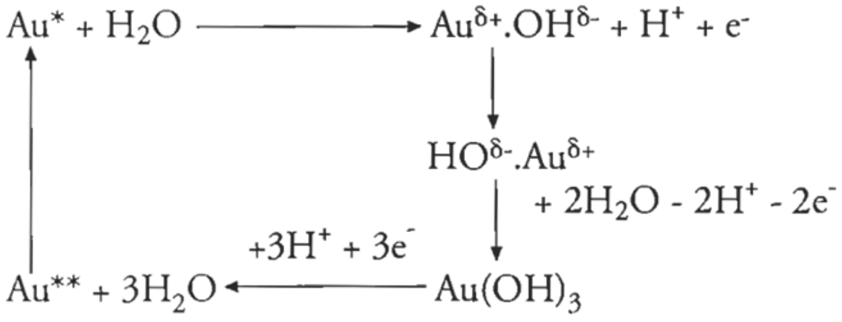


Figure2.7 Schematic of reaction of gold electrode [16]

T. C. Wen, et al. [17] compared the pure gold and gold deposited on titanium electrode by using CV techniques. They found that gold deposited on titanium gives higher current than pure gold because of crystalline structure. Pure gold had a perfect crystalline structure than the gold deposited on titanium which has the porous structure so that OH/H_2O can easily penetrate to the inner layer. Additionally, they found that the gold state (Au^{III}; after one monolayer) was not helpful in the oxidation because the surface saturations of OH/H_2O on gold resists the movement of alcohol molecules into the reactive region.

H. Erikson, et al. [18] studied the electrochemical reduction of oxygen on Au/C catalyst by varying amount of Au (20 wt% and 30 wt%). The results showed that the 20wt% Au of Au/C catalyst gives higher activity for oxygen reduction activity than 30wt% Au that corresponds to the particle size of catalyst. The 20wt% Au of Au/C catalyst had smaller Au size than the other.