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# The study of Pt@Au electrocatalyst based on Cu underpotential deposition and Pt redox replacement

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### ARTICLE INFO

Article history: Received 19 September 2008 Received in revised form 22 November 2008 Accepted 2 December 2008 Available online 6 December 2008

Keywords: Underpotential deposition Pt redox replacement Fuel cell electrocatalyst Poly-crystalline gold Formic acid oxidation

# ABSTRACT

Electrochemical study of the decorated Pt@Au catalyst synthesized by Cu underpotential deposition (UPD)-Pt redox replacement technique has been conducted in this work. The parameters affecting the Cu UPD on Au/C nanoparticles in sulfuric acid electrolyte, including the UPD potential, deposition time and potential sweep rate, were investigated in detail. Anode stripping method was used to calculate the charge of the deposited Cu adlayers. Results showed that Pt@Au catalyst prepared by this UPD-redox replacement approach is not a core-shell structure but a decorated structure. A series of decorated Pt@Au/C catalysts with various Pt coverages were synthesized and examined for formic acid oxidation (FAO). It is found that the specific activity of Pt atoms increases with the decrease of Pt surface coverage on Au. Life test showed that better stability was pertained for this decorated Pt@Au/C catalysts compared to Pt/C towards FAO.

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#### 1. Introduction

The phenomenon of underpotential deposition (UPD) has been discovered and studied for decades. Due to the stronger bond between the foreign metal adatoms with the metal substrate as compared to the same type substrate, the UPD foreign metals would deposit at a potential more positive to the Nernst potential, where bulk deposition takes place, forming one monolayer or submonolayers onto the substrate surface [1,2]. Such phenomena allow precise and reproducible control of the amount of the foreign metal adatoms on the substrate and are suitable for the study of surface coverage dependence of various systems [3]. As a result, it is very important in the surface chemistry and would make the researchers have better understandings on the initial electrodeposition process.

In recent years, Brankovic et al. [4] demonstrated a spontaneous irreversible redox replacement process, in which the UPD Cu adlayer is oxidized by more noble metal cations, e.g. Pt<sup>4+</sup>, Pd<sup>2–</sup> and Ag<sup>+</sup>, and these noble metal cations are reduced and deposited simultaneously. Finally, they could get a morphology controlled core-shell structure for catalysis application [5–12]. Since then, many researchers have applied the UPD-redox replacement technique to the synthesis of various kinds of catalysts targeting at different reactions [13–16]. Among them, of particular interest is its application to synthesize Pt based core-shell catalyst for fuel cell reactions, with an objective to reduce the usage of Pt. Tang et al. [15] prepared Pt overlayer/Au/graphite catalyst and showed high electrocatalytic activity and good long-term stability for methanol oxidation. Zhai et al. [16] prepared multiple Pt layers on Au substrate by controlling the number of UPD-redox replacement cycles and studied the influence of the Pt shell thickness to the oxygen reduction activity.

Although ideally UPD can precisely control the amount of foreign metal adlayers on the substrate, there is still something unclear about the formation of "monolayer" structure on poly-crystalline nanoparticle substrate by UPD-redox replacement technique. First, it comes from the difficulty to in-situ observe the morphology of the UPD as well as the redox replaced adlayer using microscopy. So far almost all the coupled in-situ researches with microscopy were carried out using (h, k, l) mono-crystalline surfaces as the substrate [2,4,6,10,17]. Second, the potential and time which is selected to form a monolayer in the UPD region is arbitrary. Many researchers would select an empirical potential just above that where bulk deposition commences and they claimed that they have made monolayer core-shell catalyst. Since the UPD can occur in a wide potential range, the exact UPD potential can have big effect on the resulting Cu adlayer coverage. To our experience, only several millivolts in the region close to redox potential would greatly change the resulting Cu adlayer coverage, and no complete monolayer on nanoparticle substrate can be formed before the overpotential

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<sup>0013-4686/\$ –</sup> see front matter  $\mbox{\sc 0}$  2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2008.12.004

deposition (OPD) occurs. Consequently, this will affect the structure and catalytic activity of the Pt adlayer resulting from the subsequent redox replacement. Therefore, the deposition potential and time must be chosen carefully. However, to our knowledge, there are rarely published papers addressing this point by direct electrochemical methods and evidences [18].

Here we focus on the UPD behavior of Cu deposited on the asprepared poly-crystalline Au/C substrate in sulfuric acid electrolyte and investigated the parameters affecting the Cu UPD, including the UPD potential, deposition time and potential sweeping rate. We use anode stripping method to calculate the oxidation charge associated with the UPD Cu. By comparing the UPD oxidation charge with the reduction charge of the monolayer Au oxide of the Au/C substrate, we can get the direct information between the applied potential and the surface coverage. Furthermore, a nominal Pt@Au/C "core-shell" structured catalyst was synthesized by redox replacement of the UPD Cu with K<sub>2</sub>PtCl<sub>4</sub>. Since our previous research showed that Pt-decorated Au/C catalyst possessed different electrochemical characteristics than core-shell structured Pt@Au/C [17], we verified that the as-prepared Pt@Au/C was not a perfect core-shell structure catalyst but a decorated one by formic acid oxidation (FAO). Based on that, by simply varying the UPD potential of Cu on Au/C, a series of decorated Pt@Au/C catalyst with different Pt coverage on Au/C were synthesized and their reactivity towards FAO were tested. It is noteworthy that our Pt@Au/C with 3% Pt coverage has a comparative activity with the 75% coverage sample. Bearing in mind the principle of minimizing Pt usage, the activity of the decorated Pt@Au/C with 3% Pt coverage was 20 folds more active compared to Pt/C towards FAO if the data were to be normalized by Pt usage. Finally, life test were conducted, results showed that the decorated Pt@Au/C catalyst had better stability towards FAO compared to Pt/C. The cause of the declining activity during life test was also briefly discussed.

#### 2. Experimental

#### 2.1. Preparation of nanocrystalline Au/C

The method to prepare Au/C substrate can be found elsewhere [19,20]. HAuCl<sub>4</sub>· $3H_2O$  and NaBH<sub>4</sub> was used as the gold precursor and reducing agent, respectively. As-received XC-72R carbon black was used as the support.

The metal loading was 20 wt%. The particle size was around 3.7 nm by XRD and verified by TEM (results not shown here).

# 2.2. Electrochemical test

Glassy carbon disk (PINE, USA, 5 mm diameter) was used as the working electrode; Ag/AgCl electrode (+0.197 V vs. NHE) and Pt foil were used as the reference electrode and counter electrode, respectively. All the electrochemical tests were conducted at room temperature using Autolab PGSTAT30 potentiostat (Eco Chemie, The Netherlands). The electrode potential was reported against Ag/AgCl electrode. CuSO<sub>4</sub>·5H<sub>2</sub>O (99.995%) and K<sub>2</sub>PtCl<sub>4</sub> (99.99%) are procured from Sigma–Aldrich; the electrolytes were prepared from as-received sulfuric acid (98%, Merck) and ultrapure water from Millipore MilliQ Plus system (~18.1 M $\Omega$ ).

Porous film method [21] was adopted to prepare the electrode. The catalyst slurry was prepared by supersonically dispersing 2.0 mg catalyst in 1.0 mL ethanol for 10 min, followed by the addition of 0.5 mL Nafion solution (GasHub, 5 wt% isopropanol/water suspension) with another 20 min of supersonication. Then 15  $\mu$ L of the homogenous suspension was dropped onto glassy carbon disk using microsyringe (Hamilton, USA). After drying in air, the



**Fig. 1.** Voltammetry curve for the underpotential deposition of Cu on the Au/C substrate in 0.1 M sulfuric acid with 1 mM CuSO<sub>4</sub>, sweep rate 10 mV/s. Inset: Voltammetry curve for the as-prepared 20 wt%. Au/C substrate in the absence of  $Cu^{2+}$  in 0.5 M sulfuric acid, sweep rate 100 mV/s.

electrode was mounted and immersed into the Argon (ultrapure, SOXAL) deaerated electrolyte for the electrochemical tests.

UPD tests were conducted in 1 mM  $CuSO_4 + 0.1 M H_2SO_4$  electrolyte. A typical procedure of the anode stripping test was as follows: First, the electrode was held at 0.65 V for 20 s to ensure that there was no copper on the surface, and then the potential was swept at 400 mV/s to the desired UPD potential. After certain minutes of holding time, the potential of the electrode was swept back to 0.65 V and maintained there for 60 s. Various UPD potential, deposition time and sweep rate were used to identify their effect on the resulting UPD charge.

When doing the redox replacement reaction, after holding the electrode at UPD potential in  $CuSO_4 + H_2SO_4$  electrolyte solution for 3 min, the electrode was quickly taken out of the copper electrolyte with potential control (same as the deposition potential to avoid oxidation of deposited Cu) and put into the Argon deaerated 5 mM K<sub>2</sub>PtCl<sub>4</sub>+0.05 M H<sub>2</sub>SO<sub>4</sub> solution for an arbitrary time of 10 min. Then the electrode was washed with copious ultrapure water for further tests.

FAO tests were conducted in deaerated 0.5 M HCOOH + 0.5 MH<sub>2</sub>SO<sub>4</sub> electrolyte at 1000 rpm rotation speed using Princeton Ring-Disk Electrode System (Model 636).

# 3. Results and discussion

#### 3.1. UPD studies

A typical CV curve for poly-crystalline Au could be clearly seen by the inset of Fig. 1. Burshtein method was adopted to calculate the surface area of Au/C substrate [22,23]. Normally, 1.35–1.40 V was selected as the Burshtein Minimum potential. By integrating the reduction peak at 940 mV (normally from 600 to 1150 mV), the reduction charge of Au oxide monolayer was calculated. By using the suggested value of 400  $\mu$ C/cm<sup>2</sup> for poly-crystalline Au, the real electrochemical surface area of Au/C could then be calculated.

The cyclic voltammogram for Cu UPD on poly-Au (Fig. 1) was similar to those in the literatures for Cu UPD on Au(111) [13,24]. Three peak pairs were observed. Peak pair A and A' around 0.25 V and C and C' around 0V stood for the UPD and OPD main peak pair, respectively. The small peak pair B and B' around 0.1 V was probably due to the surface structure transferring process for Cu UPD on Au(111) in sulfuric acid electrolyte [25].



**Fig. 2.** (a) Current transient during the anodic stripping process; deposition potential 0.25 V, sweep rate 400 mV/s. (b) The effect of the sweep rate on the oxidation charge of the Cu adlayer under different deposition potentials. The deposition time is fixed at 180 s. The current at the end of the oxidation sweep process for the case of 0.10 V was also shown as the dashed line. (c) Oxidation charge of the Cu adlayer vs. deposition time at different deposition potentials.

In this paper, we adopted the Steps & Sweep technique and used anode stripping method to calculate UPD adlayer charge.

After the UPD process, anode stripping was realized by sweeping the electrode potential at constant rate to the terminal potential of 0.65 V. A typical anode stripping result is shown in Fig. 2(a). It can be seen that the transient current reached the maximum at the very beginning of the oxidation process; it decayed quickly and formed a flat roof at the end of the sweeping process. The holding potential at 0.65 V was high enough to ensure that the electrode substrate was clean and free of deposited Cu. It is reasonable to assume that the effect of the pseudo double layer from the Au substrate was the same throughout the sweeping process and the current at the end of the sweeping process would be the current from the pseudo double layer capacitance only. The oxidation charge of Cu adlayer was then calculated by integrating the current after subtract the current from the double layer capacitance, as the hatched area in Fig. 2(a).

There was no doubt that the deposition potential and time were the key factors for the UPD process, while the oxidation sweep rate would also affect the calculation of the anode stripping charge of the deposited adlayers. Fig. 2(b) shows the calculated oxidization charge from the deposited Cu adlayer vs. the potential sweep rate at different deposition potentials ranging from the pure UPD region (e.g. 0.20 V) to the OPD dominated region (e.g. 0 V). It can be noticed that the oxidation charge from Cu adlayer depends on the sweep rate. From 200 to 800 mV/s, the calculated charge was stable, while when the scan rate went outside this range, the calculated charge would become smaller, especially when the scan rate was lower than 100 mV/s. When the sweep rate was too slow, due to the prolonged sweep period, more proportion of oxidation charge could not be counted in when the transient current was smaller than the double layer current. On the contrary, if the sweep rate was too fast, the time for the transient current to decay to the real current from the pseudo double layer capacitance might be too short. Both of the situations would lead to the underestimation of the calculated charge.

In order to prove our assumption that the current at the end of sweeping process would be the current from the pseudo double layer capacitance only, the charging current at the end of the potential sweeping process for the case of UPD at 0.10 V is also shown in Fig. 2(b) as a dashed line. The current vs. sweep rate was a straight line with a linear regression coefficient of 0.99862, indicating that our assumption was well applicable.

Fig. 2(c) shows the effect of the deposition time on the oxidation charges at different deposition potentials. After about 60 s when the UPD process got saturated, there were no big differences in the oxidation charges as time progressed when the deposition potential was within UPD region (0.20-0.05 V). On the other hand, deposition time would affect the oxidation charge greatly in the OPD range, because Cu OPD is not a self-terminating process and allows multilayer deposition.

Throughout this work, we took 400 mV/s and 180 s as the optimized oxidation sweep rate and deposition time.

The IV curves during the oxidation process are shown in Fig. 3(a). Only one oxidation peak could be seen when the deposition potential was higher than 0.23 V. There gradually formed a second shoulder peak when the potential was lowered. Since at this potential, OPD could not occur yet; then the shoulder peak might only reflect the structural change of the Cu UPD adlayer [2]. With the further decrease of potential, the UPD shoulder peak overlapped with the OPD oxidation peak and finally exceeded the main UPD peak (as for the case of -0.002 V) in Fig. 3(a)).

Fig. 3(b) shows the oxidation charge of Cu deposited on Au under different potentials. The monotonic increase of the oxidation charge with the decrease of deposition potential meant that there was no distinct point which separated UPD and OPD regions apart; instead, a combined region (from 0.005 to 0.015 V) set between the UPD dominant region (above 0.02 V) and the OPD dominant region (below 0 V). We could also get the same conclusion from charge calculation. In this particular case, the reduction charge of the Au surface oxide monolayer was 6.873e-4 C, while the oxidation charge of the UPD dominant region at the lowest potential of 0.02 V was 4.71827e-4 C, only about 70% surface coverage at this deposition potential. (Theoretically, the charge of a Cu monolayer on Au electrode should be the same as the reduction charge of



**Fig. 3.** (a) IV curves for anode stripping process at different deposition potentials. (b) Oxidation charge of the Cu adlayer obtained under different deposition potentials.

Au surface oxide monolayer, if both of the reactions were ideally two electron transfer reactions.) This meant that no ideal monolayer of Cu can be formed on Au nanoparticle substrate by UPD only.

There were several possible reasons for the partial covered structure. First, the atomic size difference between Cu and Au may prevent the formation of a complete monolayer. Dimitrov and coworkers [18,26] pointed out that it was theoretically impossible to deposit a real monolayer of Cu per one "building block" reaction. Second, the co-adsorbed ions from the supporting electrolyte or the trace amount of Cl- ions contamination from the reference electrode might influence the structure of the Cu UPD adlayer, because halogen ions strongly absorbed on Au surface and weakened the Cu-Au bond [17]. Recently, Martinez-Ruiz et al. [24] reported that on Iodine modified Au(111) substrate in sulfuric acid electrolyte, Cu could not form a full monolayer before OPD took place. Third, the morphology effect of the porous Au/C substrate might also play a role. From the reduction charge of the Au oxide and the reported value of 400  $\mu$ C/cm<sup>2</sup>, the surface roughness factor of the Au/C electrode prepared by the porous film method was calculated at the range of 6-10. Some of the Au atoms on the rough surface might not be accessible by the Cu ions.

# 3.2. Decorated Pt@Au/C

Although we cannot make a real monolayer of Cu on Au, the study of Cu UPD reminded us that we could synthesize a series of

decorated catalysts with different surface coverages by fine tuning the deposition potential during the UPD process.

Here we focused on the decorated Pt@Au/C catalyst for FAO reaction. Recently, we reported that Pt-decorated Au/C catalyst synthesized by a two-step chemical approach had enhanced activity towards FAO [19]. This enhanced activity is believed to result from the ensemble effect that a single Pt atom would have much higher activity compared to the bulk Pt clusters [27]. In this work, we adopted the UPD-redox replacement technique, to get the decorated Pt@Au/C catalysts with controlled Pt coverages and to test their activities towards FAO. The nominal Pt coverage was calculated as the ratio of the charge from Cu adlayer oxidation and that of the Au oxide reduction. Here, we assume that the efficiency of the redox replacement reaction of Cu atoms by Pt ions was 100%. During these experiments, the current density could not be normalized by the hydrogen desorption peak charge from the CV in the sulfuric acid electrolyte, because it is not accurate anymore to calculate the electrode surface area by Pt alone for these decorated bi-metal catalysts. Instead, the current density was normalized by the Au electrode surface areas.

Fig. 4 shows the forward voltammograms of the FAO on a series of decorated Pt@Au/C with different surface coverages. The inset of Fig. 4 shows the CV curves in blank 0.5 M H<sub>2</sub>SO<sub>4</sub>. A gradually decreased Pt surface area with the decrease of the nominal Pt coverage could be clearly seen through the hydrogen adsorption/desorption area, which indicates the success on controlling the amount of Pt on Au/C by using UPD-redox replacement technique.

As could be seen in Fig. 4, the second anodic dehydration peak around 0.75 V decreased with the lowering of the total Pt amount, and finally diminished when the Pt coverage was below 34%, suggesting that oxidation of the formic acid would be shifted to the dehydrogenation branch to form CO<sub>2</sub> while CO poisoning was gradually suppressed with the lowered Pt coverage. One thing should be noticed that even for the minimum coverage of Pt (3%) on Au in this study, the forward scan peak current density reaches 68% of that of the 75% coverage sample (the sample with the highest activity). This meant that much higher activity per Pt atom towards formic acid oxidation could be achieved with only a little amount of Pt. To quantify the specific activity of Pt atoms towards formic acid oxidation, the measured CV peak current at 0.3 V was also normalized by the total number of Pt atoms (Au itself has negligible activity) and the results are shown in Table 1. It was found that the specific activity of Pt atoms increased with the decreased of Pt surface coverage. The 3% coverage Pt@Au/C sample showed 17.0 and 23.9 folds



**Fig. 4.** Voltammogram of as-prepared Pt@Au/C with different Pt coverages in 0.5 M formic acid and 0.5 M  $H_2SO_4$ , sweep rate 100 mV/s, rotation speed 1000 rpm. The current density is normalized with the Au electrode surface area.

### Table 1

Normalized peak current for formic acid oxidation on Pt atoms.					
Nominal Pt coverage (%)	100	75	34	14	

 Nominal Pt coverage (%)
 100
 75
 34
 14
 3

 Peak current per Pt atom
 0.4335
 0.611
 1.225
 2.189
 10.373

 (10<sup>-18</sup> A/atom)

 10.373

more active towards FAO compared to the 75 and 100% coverage samples, respectively.

Since the decorated Pt@Au/C catalyst has much lower tendency towards CO poisoning, it may have better stability during the FAO life test. However, on the other hand, it is well known that Pt/Au system is strongly segregated and Pt is easily covered by Au, which may mark the end of the catalyst. The overall durability of the decorated catalyst depends on both factors. To get more information about the durability, the short-term stability of the catalyst towards FAO was investigated by two approaches and the results were compared with 20 wt%. Pt/C sample made by EG method (particle size around 4 nm, the synthesis method could be found elsewhere [28]).

First, a prolonged CV tests up to 2000 cycles were conducted. As could be seen in Fig. 5, the activity towards FAO of the Pt/C catalyst always decreased as the test continued; while for the 3% coverage Pt@Au/C sample, before 200 cycles of CV, the activity did not change too much (it actually slightly increased). After 200 cycles, the activity started to decrease with a very fast declining rate. Nevertheless, the activity of 3% Pt@Au/C at the end of 2000 cycles is still better than 20% Pt/C. The CV results in blank 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte



Fig. 5. Prolonged CV results of (a) 3% Pt@Au/C (b) Pt/C in 0.5 M formic acid and 0.5 M H<sub>2</sub>SO<sub>4</sub>, sweep rate 100 mV/s, rotation speed 1000 rpm. Only the forward scans were shown.



Fig. 6. CV results of (a) 3% Pt@Au/C (b) Pt/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> before and after prolonged CV test. Sweep rate 100 mV/s, rotation speed 1000 rpm.

before and after the prolonged CV tests are shown in Fig. 6. The active surface area of both catalysts showed a continuous loss. The activity decline of the catalysts was mainly due to the active surface area loss of Pt. For the decorated catalyst, it is surprising that the activity did not decline although the Pt surface area dropped significantly from 0 to 200 cycles. As evidenced by the negligible hydrogen desorption area, most of the active surface area was lost after 500 cycles, probably caused by the strong segregation of Pt/Au system or the dissolution of Pt. However, at such low Pt loading, it might not be accurate to quantify the Pt amount using the hydrogen desorption area. Indeed, the Pt oxide reduction peak was still detectable after 500 cycles and showed a negative shift in peak position. This negative shift could be explained by the upper shift in the Pt d-band center, which leads to a higher adsorption energy of adsorbate, oxygen containing species in this case [29].

Chronoamperometric experiments were also conducted at the potential of 0.15 V and the results are shown in Fig. 7. The gradual current decay was due to both the Pt surface area loss and CO poisoning effect. The activity loss due to surface area loss is permanent and could not be resumed anymore. To quantify the effect due to CO poisoning, an electrode cleaning procedure was introduced during the chronoamperometric experiment, where the electrode was first held at 0.9 V for 10 s, then at -0.2 V and 0.75 V for 1 s to clean the catalyst surface. After that, the electrode was held at the life test potential of 0.15 V for another 20 min. The short life test duty cycle was repeated twice to see whether the reactivity could be resumed. As could be seen, the current decreased quite fast in the very beginning of the CA test, while it could be resumed after the surface cleaning procedure for both catalysts. However, the 3%



Fig. 7. Life test of 3% Pt@Au/C and Pt/C in 0.5 M formic acid and 0.5 M H<sub>2</sub>SO<sub>4</sub> underpotential of 0.15 V, rotation speed 1000 rpm. Current densities are normalized by the calculated electrochemical surface area of Pt.

coverage of Pt@Au/C sample had much lowered declining rate compared to the Pt/C catalyst. For Pt/C catalyst, it would suffer from the CO poisoning and cause activity decline from the very beginning of the test. While for the decorated Pt@Au/C sample, it had much less CO-like species formed in the beginning and the accumulation of CO is also much slower. The much alleviated CO poisoning effect makes the decorated Pt@Au/C sample more capable to catalyze FAO compared to Pt/C catalyst.

#### 4. Conclusions

The charge of the Cu adlayer deposited on the as-prepared polycrystalline Au/C nanoparticles was calculated by anode stripping method. Results showed that under the current experiment condition, i.e. in sulfuric acid supporting electrolyte and using the porous film electrode, we could not get an ideal fully covered monolayer of Cu adlayer underpotentially deposited on Au/C nanoparticles before OPD started.

Based on that, various decorated Pt@Au/C catalyst with tunable Pt coverage were synthesized by using UPD-redox replacement technique. The decorated Pt@Au/C catalyst showed much higher activity towards formic acid oxidation than that of Pt/C. Particularly, the highest specific activity was obtained in the case of the minimum Pt coverage (3% in this study). Moreover, the decorated Pt@Au/C catalyst showed better stability than the Pt/C towards FAO due to the suppressed CO poisoning species formed on Pt. The apparent advantage of the catalyst prepared by this approach is the significant reduced Pt usage. With all the Pt atoms existing on the surface, electrochemically available and possessing high specific activity, this catalyst is promising to be used in formic acid fuel cell applications.

### Acknowledgements

This work is supported by Academic research fund AcRF tier 1(RG40/05) and AcRF tier 2 (ARC11/06), Ministry of Education, Singapore.

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