REACTION KINETICS OF Cu ELECTRO-DEPOSITION ON THE SURFACE OF TiO₂/GRAPHITE

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ABSTRACT

Research on the kinetics of electrode reaction during copper electro-deposition on the surface of TiO₂/graphite has been conducted. The aims of this research are to determine the ratio of anodic reaction rate to cathodic reaction rate $\left(\frac{\overline{ra}}{\overline{rc}}\right)$, the ratio of anodic rate constant to cathodic rate constant $\left(\frac{\overline{ka}}{\overline{kc}}\right)$, the equilibrium constant when the reaction reach equilibrium condition and to study the polarization in the electro-deposition reaction. Copper was deposited electrochemically from CuSO₄ solution at various concentration i.e. 0.1 M; 0.2 M; 0.3 M; 0.4 M; 0.5 M. In every 5 minutes during electro-deposition process, the pH changes in anode cell was recorded and the change of Cu²⁺ concentration was also analyzed by spectrophotometric method. The result shows that the reaction order of Cu²⁺ reduction is first order and the oxidation of H₂O in anodic cell is zero order. The ratio of anodic rate constant to cathodic rate constant $\left(\frac{\overline{ka}}{\overline{kc}}\right)$, is $4.589 \times 10^{-3} \pm 0.071 \times 10^{-3}$. It indicates that the reaction rate in cathode is larger than the reaction rate in anode and it allowed polarization. The electrochemical cell reached equilibrium after 25 minutes with the equilibrium constant is $8.188 \times 10^{-10} \pm 1.628 \times 10^{-10}$.

Keywords: Cu Electro-deposition, TiO₂/Graphite, Kinetics of electrode reaction.

INTRODUCTION

Semiconductor materials play important role in human life such as for photocatalyst, sensor, electronic devices or solar cells. The photocatalyst powders have been applied for photocatalytic treatment of waste water, degradation of dye waste, disinfection treatment of water or fabrics etc. The immobilized form of photocatalyst such as in the form of thin layer on substrat has been studied intensively in order to reduce post treatment cost of separation between the product of photocatalytic degradation and its photocatalyst powder and also the immobilized form is easier to be recycled.

Immobilization of photocatalyst on a substrat has been investigated by some researchers

such as Yang *et al.*^[1] who succesfully grown mesoporous silica layer on graphite with the presence of surfactant cetyltrimethyl-ammonium chloride (CTACl). The deposition method by using surfactant as linking agent is an innovation due to the method is unexpensive, no requirements of specific equipment and high temperature. Rahmawati *et al.*^[2] also deposited TiO₂ film by chemical bath deposition with the assistance of surfactant molecules of cetyl trimethyl ammonium borate (CTAB).

TiO₂ is a photo-catalyst for multivarious activities, in which the most promises property is its photocatalytic behaviour^[3] and relatively more chemically stable than other oxide materials^[4]. TiO₂ has been applied as photocatalyst to solve some environmental

problems such as purification of water and air, destruction of microorganisms and inactivation of cancer cells^[5]. TiO₂ possesses several prominent advantages including high chemical resistance under highly acidic or basic medium, high mechanical strength that reduces the risk of breaking during reaction^[6].

The performance as photocatalyst can be reduced due to the recombination phenomena between the excited electrons and the positively leaving holes⁷. Therefore some reseachers did some efforts to reduce the recombination phenomena, such as by combining with other semiconductor to form coupling semiconductor, depositing metal on the semiconductor surface etc. Metal surface deposition has proven can increases the photocatalytic activity of TiO₂ by reducing the recombination phenomena. The deposited metal can serves as electrons trapper and allows the holes to migrate to the surface of semiconductor and act as oxidator for the targeted molecules. Meanwhile, the electrons that carry the negative charge can act as reductor. In order to deposite metal on the semiconductor surface, there are many methods that can be used such as chemical deposition, sputtering, coating or electro-deposition. In this research, the electro-deposition method was chosen due to the TiO₂ layer was deposited on a conductive substrate, i.e graphite. The conductive property of graphite allows an electro-assisted deposition is possible to be applied. The preparation of TiO₂ layer on graphite was conducted by chemical bath deposition as it was conducted in our previous researches^[2,8]. Graphite was also used as catalyst supports^[9]. Meanwhile, Zhu *et al.*^[10] used carbon—titania composite as catalyst support.

The electro-deposition of Cu from CuSO₄ solution has been conducted previously by our group and showed that the Cu deposition increases the photocatalytic activity of TiO₂/Graphite^[2]. It was found that electro-deposition of Cu on TiO₂/Graphite did not follow Faraday's Law as it described in equation (1) that the weight of deposited metal is in linear relationship with the applied current and time of electro-deposition. This research investigated whether the deviation from Faraday's law is

caused by the Cu²⁺ reduction into Cu reaches equilibrium after a definted time or it is caused by loss of the deposited Cu. Therefore, in this research the concentration of Cu²⁺ during electro-deposition process was measured continuously at every definted time by using UV-Vis spectroscopy. Meanwhile, the proceed of anodic reaction was recorded through pH measurements. The pH value is refer to the concentration of H⁺ which was produced by oxidation reaction of H₂O.

$$W = \frac{M.i.t}{n.96500} \quad (1)$$

Where gw is the weight of the deposited metal (g), *M* is the relative molecular mass(g.mol⁻¹), *n* is the number of electrons involved in the reaction, *i* is the applied current (Ampere), *t* is time of electro-deposition (second) and 96,500 is the Faradaic constant.

MATERIALS AND METHODS

Titanium (IV) chloride (Merck) was used as titanium dioxide precursor, the graphite rods from ABC battery industry were sliced into tablets and used as substrate for TiO₂ layer. The TiO₂ layer was coated on graphite substrate by chemical bath deposition method (CBD) at acidic condition of HCl 37% and the surfactant molecules of cetyl trimethyl ammonium bromide (CTAB). Cu was deposited from CuSO₄ solution which was prepared by dissolving CuSO₄.5H₂O (Merck) in deionized water.

The graphite tablets were heated at 105 °C for 1 hour. After being cooled at room temperature, the discs then to be weighing analytically. Those gravimetrical procedure were conducted until the weight of graphite disc is constant (the weight different is less than 0.02 g). After the gravimetrical weighing of the graphite discs were noted, TiO₂ layer then to be coated on graphite disc by CBD method. A 100 mL solution that contain of 8.3 mL of 1 M HCl solution and 1.1 mL of 1 M TiCl₄ solution was prepared as the precursor for TiO₂ layer. The detail procedure on TiO₂ layer preparation is

described our previous paper⁸. The produced $\text{TiO}_2/\text{graphite}$ was then to be characterized by X-ray diffraction (Shimadzu 6000) to analyzed its phases and its crystallinity.

The electro-deposition was conducted by using Analytic Analyzer Electrolysis Yanaco AES-2D with accuracy of 1×10^{-2} volt. A digital multimeter, Fluke 73 Series was used to record electrical current pass through the electrochemical cell, the potential of cathode and the potential of anode at every 5 minutes. Cu was deposited from a series of CuSO_4 solution i.e. 0.1 M; 0.2 M; 0.3 M; 0.4 M and 0.5 M. The $\text{TiO}_2/\text{graphite}$ was used as cathode and a graphite rod was used as anode. A constant current of 0.02 A was applied to the electrochemical cell. A glass electrode of pH meter was dipped into the electrochemical cell to record the pH of water as the result of oxidation of H_2O . Meanwhile, in every 5 minutes, Cu^{2+} concentration was measured by using UV-Vis spectrophotometer, double beam Shimadzu 1601 PC. The light wavelength of maximum absorbance of CuSO_4 solution was determined and it was 810 nm. Then, a standard absorbance curve of CuSO_4 solution was plotted. The curve was used to determine the Cu^{2+} concentration from its absorbance values. The design of electro-deposition cell is described in Figure 1. The prepared Cu- $\text{TiO}_2/\text{graphite}$ then to be weighted gravimetrically. The kinetics study on the electrode reactions were carried out by determining the comparison of anodic reaction rate to cathodic reaction rate (r_a/r_c)

and the ratio of anodic reaction rate constant to cathodic reaction rate constant (k_a/k_c). Each experiment was conducted three times (triple).

RESULTS AND DISCUSSION

In order to analyse the TiO_2 layer that was deposited by CBD method on graphite substrat and the Cu deposit on $\text{TiO}_2/\text{Graphite}$, the prepared materials were analyzed by X-ray diffraction at 2θ of 10° - 90° . The diffraction patterns are depicted in Figure 2.

The diffraction pattern of the prepared materials, Figure 2, were compared to the d spacing values of anatase TiO_2 and rutile TiO_2 standard diffraction according to JCPDS #. It was found that the prepared TiO_2 layer is present in anatase and rutile. Highest anatase peak is at 2θ 54.1441° and the highest rutile peak is at 2θ 43.8402° . The Cu peaks are identified at 2θ 43.37° , 2θ 50.60° and 2θ 74.22° . The peaks were identified based on Cu standard diffraction ICSD# 43493. Scherrer equation was used to estimate the crystallite size of particles, and showed that the crsyallite size of rutile is 9.74 nm, the crystallite size of anatase is 9.75 nm and the deposited Cu is 26.32 nm.

The redox (reduction-oxidation) reaction during electro-deposition are as listed in equation (2) and (3).

Figure 1. The scheme of electro-deposition cell.

Figure 2. The diffraction patterns of a) TiO₂/graphite and (b) Cu-TiO₂-graphite. R is rutile, A is anatase and Cu is copper peak.

Cathodic reaction:

Anodic reaction:

Total reaction:

After 25 minutes of electro-deposition, the absorbance of Cu²⁺ solution was constant, as it is described in Figure 3. It indicates that the reaction of Cu²⁺ into Cu reached equilibrium after 25 minutes. Therefore, the reaction kinetics study was conducted on the data before 25 minutes of electro-deposition time.

The determination of reaction order was conducted by plotting ln A versus t (minutes) for first order and 1/A versus t (minutes) for second order. The suitable reaction order was chosen based on the value of linearity

constant, R, which are listed in Table 1. The graphics of and its linear equations are depicted in Figure 4.

Figure 3. Plot of A versus time during Cu electro-deposition from (a) 0.1 M of CuSO₄ solution and (b) 0.2 M of CuSO₄ solution.

Table 1. The linearity constants of first order and second order plot

[Cu ²⁺] (Molar)	R ² (1 st order)	R ² (2 nd order)
0.1	0.9996	0.9993
0.2	0.9998	0.9996
0.3	0.9998	0.9996
0.4	0.9999	0.9995
0.5	1.0000	0.9999

The electrochemical kinetics study of Cu deposition was described according to Buttler-Volmer equation (equation (4)) [10].

$$j = j_o \left\{ \exp \left[(1 - \alpha) \frac{nF}{RT} \eta \right] - \exp \left[-\alpha \frac{nF}{RT} \eta \right] \right\} \quad (4)$$

Where j represents the current density, η is the overpotential, j_o is the exchange current density, n is the number of exchanged electrons, T is the temperature and α is the cathodic transfer coefficient or named as symmetric factor. If the cathodic transfer coefficient is 0.5, therefore the anodic transfer coefficient will also 0.5. It means that the symmetrical factor of the electrochemical reaction is 0.5.

By considering that symmetric factor is 0.5 for anode reaction and 0.5 for cathode reaction, therefore the electrode reaction rate were calculated by equation (5) and (6). The equations are derived from the reaction rate as described in Prentice [11].

$$ra = k'_a C_R \exp \left\{ \frac{0.5nF\Phi}{RT} \right\} \quad (5)$$

$$rc = k'_c C_o \exp \left\{ \frac{-0.5nF\Phi}{RT} \right\} \quad (6)$$

Where ra is the anodic reaction rate, rc is the cathodic reaction rate, n is the number of electrons contribute into the reaction, F is Faradaic number, R is the gas constant, T is temperature, C_R is the concentration of

reduced species, C_o is the concentration of oxidized species and Φ is the potential of electrode during the reaction. Meanwhile, the anodic rate constant, ka , and the cathodic rate constant, kc , are expressed by equation (7) and (8).

$$ka = k'_a \exp \left\{ \frac{(1 - \beta)nF\Phi}{RT} \right\} \quad (7)$$

$$kc = k'_c \exp \left\{ \frac{-\beta nF\Phi}{RT} \right\} \quad (8)$$

Where β is symmetrical factor with values range from 0 – 1. It is a fraction of potential different in the electrical double layer of cathodic reaction. The value is usually 0.5, with the assumption that anodic and cathodic are symmetrical. If the value of β is zero, it means that there are no energy promoted in cathodic reaction [11].

By substituting equation (7) into (5) and (8) into (6), therefore the ratio of anodic reaction rate and cathodic reaction rate can be expressed as equation (9).

$$\frac{r_a}{r_c} = \frac{k_a}{k_c} \frac{C_R}{C_o} \quad (9)$$

r_a/r_c is the ratio of anodic reaction rate and cathodic reaction rate, C_R is concentration of the reduced species, which is Cu²⁺ and C_o is concentration of the oxidized species, which is H₂O. The ratio of anodic reaction rate to cathodic reaction rate, ra/rc are listed in Table 2.

Meanwhile, reaction order of H₂O in anodic reaction was determined from linear plotting of H₂O concentration against/versus time, before the reaction reach equilibrium. The H₂O was determined based on pH data during reaction which represented the H⁺ concentration, [H⁺]. Based on equation (3) it is known that the concentration of H₂O that oxidized into O₂ and H⁺ is similar to 0.5 times [H⁺]. The calculation results are listed in Table 3. Table 3 shows that the anodic reaction is proceed with zero order with rate law described in equation (10).

$$r_a = k_a [H_2O]^0 = k_a \quad (10)$$

Figure 4. Plot to determine the reaction order (a) first order plot and (b) second order plot.

Tabel 2. The ratio of anodic reaction rate, r_a to cathodic reaction rate, r_c .

$[\text{Cu}^{2+}]$ concentration (Molar)	$\overline{r_a/r_c}$ experiment 1	$\overline{r_a/r_c}$ experiment 2	$\overline{r_a/r_c}$ experiment 3	The average $\overline{r_a/r_c}$
0.1	3.755×10^{-2}	4.044×10^{-2}	3.582×10^{-2}	3.794×10^{-2}
0.2	3.147×10^{-2}	2.487×10^{-2}	3.138×10^{-2}	2.924×10^{-2}
0.3	2.061×10^{-2}	2.302×10^{-2}	2.160×10^{-2}	2.174×10^{-2}
0.4	8.646×10^{-3}	9.551×10^{-3}	8.691×10^{-3}	8.963×10^{-3}
0.5	8.856×10^{-3}	9.716×10^{-3}	8.850×10^{-3}	9.141×10^{-3}

Meanwhile, reaction order of H_2O in anodic reaction was determined from linear plotting of H_2O concentration against/versus time, before the reaction reach equilibrium. The H_2O was determined based on pH data during reaction which represented the H^+ concentration, $[H^+]$. Based on equation (3) it is known that the concentration of H_2O that oxidized into O_2 and H^+ is similar to 0.5 times $[H^+]$. The calculation results are listed in Table 3. Table 3 shows that the anodic reaction is proceed with zero order with rate law described in equation (10).

$$r_a = k_a [H_2O]^0 = k_a \quad (10)$$

The anodic reaction rate is similar to the value of its reaction rate constant, k_a . If the reaction rate is determined from the production of H^+ which was recorded during electro-deposition process, therefore, the linear regression plot of $[H^+]$ versus time produces slope which represent the rate constant, k_a . Table 4 shows the ratio of anodic rate constant to cathodic rate constant, k_a/k_c . Cathodic reaction rate constant, k_c , was determined from slope value of plot between absorbance of Cu^{2+} solution over time (minutes).

The ratio of anodic rate constant to cathodic rate constant as listed in Table 4, show that the cathodic reaction was proceed faster than anodic reaction. In general the electro-deposition of metal usually has high current density exchange. The result of this

experiment shows that the ratio of anodic reaction rate to cathodic reaction rate is not 1, therefore the total electrochemical reaction of Cu electro-deposition is concluded to be polarized. The polarization that caused by the difference in reaction rate is known as kinetic polarization.

In this research the potential of half cell anode and half cell cathode were recorded in order to study the redox reaction at equilibrium condition and observed that after 25 minutes the Cu^{2+} absorbance was constant, which indicated that the reaction has reached equilibrium. The half cell potentials are listed in Table 5. It shows that the half anode, half cathode and the cell potentials were increased as the concentration of Cu^{2+} was increased. This result is in agreement with equation (11) and (12) in which the cathode potential, $E_{cathode}$ is increased as the $[Cu^{2+}]$ increase, meanwhile the anode potential, E_{anode} is reversed to $[H^+]$ or it is increased when the pH of electrolyte solution is increased. The $[H^+]$ increased as the $[Cu^{2+}]$ was increased. However, during electro-deposition, the pH of solution was decreasead which indicated the production of H^+ .

$$E = E^o + \frac{RT}{2F} \ln a_{Cu^{2+}} \quad (11)$$

$$E = E^o - \frac{RT}{nF} \ln \frac{a_{H^+}^2 \cdot a_{O_2}^{1/2}}{a_{H_2O}} \quad (12)$$

Table 3. The pH of solution and the concentration of H_2O during anodic reaction before it reached equilibrium.

T (minutes)	pH	$[H^+]$ M	$[H^+]_n - [H^+]_o = 2\alpha$	α	$[H_2O]$ M = $[H_2O]_o - \alpha$
5	4.39	4.07×10^{-5}	0.76×10^{-5}	0.38×10^{-5}	5.73×10^{-5}
10	4.21	6.17×10^{-5}	2.86×10^{-5}	1.43×10^{-5}	5.73×10^{-5}
15	4.04	9.12×10^{-5}	5.81×10^{-5}	2.91×10^{-5}	5.73×10^{-5}
20	3.86	1.38×10^{-4}	10.49×10^{-5}	5.25×10^{-5}	5.73×10^{-5}
25	3.71	1.95×10^{-4}	16.18×10^{-5}	8.09×10^{-5}	5.73×10^{-5}

Table 5. Half cell potential of anode and cathode

[Cu ²⁺] M	E _{cathode} (Volt)	E _{anode} (Volt)
0.1	0.532	1.415
0.2	0.543	1.429
0.3	0.558	1.442
0.4	0.569	1.452
0.5	0.575	1.464

The equilibrium constant was determined based on Nernst equation (equation (13)). The half cell potentials that are listed in Table 5 were used to calculate the anodic E' value and cathodic E' value by using equation (13) and (14). The standar half cell potential, E_{anode} was determined from linear plotting of E' versus H⁺ concentration which was calculated from pH of solution. Meanwhile, E_{cathode} was determined from linear plotting of E' versus CuSO₄ concentration (equation (14) and equation (15)). The standar cell potential, E^o_{cell}, was calculated by using equation (16).

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln K \quad (13)$$

$$E' = E + \frac{2.5RT}{2F} \ln [H^+] \quad (14)$$

$$= E^o - \frac{RT}{nF} \ln 0.5 - \frac{RT}{nF} \ln \gamma_{H^+}^{2.5}$$

$$E' = E - \frac{RT}{2F} \ln [Cu^{2+}] \quad (15)$$

$$= E^o + \frac{RT}{nF} \ln [Cu^{2+}]$$

$$E_{cell}^o = E_{Cu^{2+}/Cu}^o + E_{H_2O/H^+}^o \quad (16)$$

As the E' and E^o were able to be determined, therefore the activity coefficient, γ , can be calculated by equation (14) for H⁺ and by equation (14) for Cu²⁺. Then the activity of each ions can be calculated by equation (17) and the equilibrium constant, K, was determined by equation (18).

$$a_i = \gamma_i \cdot m_i \quad (17)$$

$$K = \frac{a_{O_2}^{1/2} \cdot a_{H^+}^2 \cdot a_{Cu}}{a_{Cu^{2+}} \cdot a_{H_2O}} \quad (18)$$

γ_i is the activity coefficient of species i and m_i is molality of species i and a is the activity of each species in the solution. The equilibrium constants are listed in Table 6.

CONCLUSION

The electrochemical reaction of Cu deposition reach equilibrium after 25 minutes. The reaction order of cathodic reaction is 1 and zero order for H₂O in anodic reaction. The ratio of anodic rate reaction to cathodic rate reaction, $\left(\frac{\overline{ra}}{\overline{rc}}\right)$ and the ratio of its reaction rate constant, $\left(\frac{\overline{ka}}{\overline{kc}}\right)$ show that the cathodic reaction proceed faster than anodic reaction or the electrochemical cell was under kinetic polarization.

Table 6. The equilibrium constants, K of redox reaction in the electrochemical cell at various concentration of CuSO₄ solutions.

[Cu ²⁺] M	K _I	K _{II}	K _{III}	The average, $\overline{K}$
0.1	1.423×10 ⁻⁹	1.456×10 ⁻⁹	1.346 ×10 ⁻⁹	1.408×10 ⁻⁹
0.2	1.105×10 ⁻⁹	1.065×10 ⁻⁹	1.044 ×10 ⁻⁹	1.071×10 ⁻⁹
0.3	4.495×10 ⁻¹⁰	7.592×10 ⁻¹⁰	6.501×10 ⁻¹⁰	6.196×10 ⁻¹⁰
0.4	3.621×10 ⁻¹⁰	5.663×10 ⁻¹⁰	7.391×10 ⁻¹⁰	5.558×10 ⁻¹⁰
0.5	3.296×10 ⁻¹⁰	6.123×10 ⁻¹⁰	3.774×10 ⁻¹⁰	4.398×10 ⁻¹⁰
$\overline{K}$				8.188×10 ⁻¹⁰ ±1,628×10 ⁻¹⁰

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