

Facile electrogenerative deposition of Au nanoparticles on a reticulated vitreous carbon electrode at various pH values for the electrooxidation of ethanol

Fatemeh Salehi Karoonian,

Mohammad Etesami,

Norita Mohamed*

*School of Chemical Sciences,
Universiti Sains Malaysia,
11800 Minden, Penang, Malaysia*

The present report aims at investigating the deposition of gold onto reticulated vitreous carbon (RVC) from a solution that contains AuCl_4^- ions and sodium chloride as a supporting electrolyte at different pH values. Thermodynamic parameters of the system were obtained. Evaluation of these parameters indicates that the exothermic gold deposition reaction tends to proceed spontaneously. The results showed that pH 3 is the most favoured condition for gold electrodeposition in terms of deposition rate and reducing anode usage. The grains of gold on RVC at pH 1 were smaller and more homogeneous. This fine structure offers the possibility of Au supported substrate to be used for catalytic applications. By increasing pH from 1 to 7, the spherical grains formed aggregates and tended to form sponge shaped gold at pH 7. The use of AuNPs/RVC as a catalyst for the ethanol oxidation was investigated.

Key words: electrocatalyst, ethanol oxidation, gold electrodeposition, pH, reticulated vitreous carbon

INTRODUCTION

Gold nanoparticles (NPs) are well known as a catalyst for the electrooxidation of some organic compounds which has attracted much attention in fuel cell applications [1]. Due to the unique characteristics of gold such as excellent corrosion resistance and high electrical conductivity, it has become a significant material for both industrial and medical purposes, which has increased the annual gold demand with many applications in catalysis, electronic industry, and biological systems [2]. Inert catalyst supports are mostly favoured in the preparation of NPs. Several polymeric or carbon based materials have been used due to their high conductivity and stability [1, 3, 4]. Various catalysts have been used for the electrooxidation of small organic compounds such as alcohols [5–7] and amongst them AuNPs electrodes have shown

satisfactory performance in recent studies [4, 8–11]. The best catalytic activity of gold electrode is usually observed in alkaline medium [12, 13]. Gold can be deposited from various sources such as leachate of refractory gold ore [14], electronic parts [15], and from industrial waste solutions [16–18]. To date, various systems and techniques have been designed and developed for gold deposition from aqueous solutions [19–22]. The method used should be chosen based on the kinetics and thermodynamics of the system as well as the operating cost. One of the proposed methods is metal deposition by an electrogenerative process [23, 24], which is potentially more favourable due to its low energy requirements, simplicity and providing a cheap and clean system. In gold deposition in acidic media using gold-chloro complexes, the rate of deposition depends on the hydrogen ion and chloride ion concentrations [22]. Hence by reducing the pH value, the metal deposition efficiency is enhanced due to the formation of more stable gold complexes which leads to a decrease in the hydrolysing

* Corresponding author. E-mail: mnorita@usm.my

side reactions involving gold-chloro complexes. The rate of hydrogen evolution will increase by decreasing pH. This phenomenon has a very high impact on the morphology of gold deposited. The pH of the solution also plays an important role in the speciation of gold compounds [25–27], stability of gold compounds [28], gold morphology [27, 29] and its uptake [30]. Gold speciation has been studied in different media and the products of its hydrolysis over different pH ranges have been reported [28]. Although the importance of pH on the immobilization of heavy metals in different systems has been reported [31], to the best of our knowledge, there has been no record on the electrodeposition of gold from chloride media using such an electrogenerative system that we present in this work. The deposition performance has been discussed based on thermodynamic and kinetic considerations.

The exclusive characteristics of reticulated vitreous carbon (RVC) [32] as a three-dimensional material offer favourable applications in electrocatalytic studies. In addition, the electrodeposition of precious metals on the RVC surface can highly improve its catalytic activity [33] because of its unique characteristics such as providing larger surface area. The oxidation of alcohols due to their significant applications has been widely studied [4, 9, 34, 35]. In this research due to achieving fine Au NPs on the RVC substrate at pH 1, the electrooxidation of ethanol with the AuNPs/RVC cathode was also investigated.

EXPERIMENTAL

Materials

Hydrogen tetrachloroaurate trihydrate (III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (purity > 99.9%) was obtained from Sigma-Aldrich and NaCl was used as the supporting electrolyte. Sodium dihydrogen phosphate (NaH_2PO_4), ethanol and other chemicals were all of the analytical grade. Anion exchange membrane Neosepta AM-01 (Tokuyama Corp.) was used to separate the anolyte and catholyte compartments. The anode was pure zinc (99% purity) of dimensions $2 \times 5 \times 0.05$ cm. The cathode used for gold deposition was 80 pores per inch (ppi) RVC (The Electro-synthesis Co.).

Apparatus and procedure

Gold deposition studies

A batch cell which was used for the electrogenerative deposition of gold consisted of two electrolyte compartments separated by an anion exchange membrane. Copper sheets which were used as current collectors were directly connected to the electrodes. The current collectors were connected by an external conducting wire to complete the circuit. A saturated calomel electrode (SCE) with a Luggin capillary was used as a reference electrode.

To study the electrodeposition of gold and evaluate the thermodynamic parameters of gold deposition, 250 mg L^{-1} Au(III) and $2.00 \times 10^{-1} \text{ M}$ NaCl were used as a catholyte and 0.1 M NaCl was used as an anolyte. In order to maintain the

pH of the solutions at the desired value, 0.4 M sodium dihydrogen phosphate was used in both catholyte and anolyte solutions. The pH was adjusted to values of 1, 3, 5 and 7 by adding drops of NaOH or HCl solutions. One hundred milliliters of catholyte and anolyte were used in each compartment.

Atomic absorption spectroscopy (Perkin Elmer AAnalyst 200) was used to determine the metal ion concentrations of the sampled catholyte solutions as a function of time during the electrodeposition process. The experiments were done at least in triplicate.

The UV-Visible spectra of the gold solution were observed with a UV-Visible spectrometer (Perkin Elmer Lambda 35). The surface morphology and characterization of the gold deposits were visualized through scanning electron microscopy (SEM) (Leo Supra 50 VP) equipped with an Energy-Dispersive X-Ray analysing system (EDX) and X-Ray diffraction (XRD). The batch cell was placed in a water bath at different temperature, and E_{cell}° was measured at different temperatures.

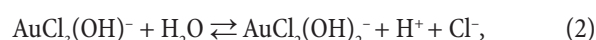
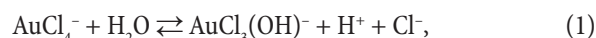
Ethanol oxidation

An eDAQ EA 161 potentiostat connected to an e-corder 410 (4-channel recorder) equipped with the EChem software was used to carry out the electrochemical studies. Prior to each run, the system was deoxygenated by aerating with nitrogen gas. The catalytic performance of the prepared AuNPs/RVC (as a working electrode) was investigated by cyclic voltammetry and platinum wire and silver/silver chloride (3M KCl) were used as counter and reference electrodes, respectively, using a conventional three-electrode cell.

RESULTS AND DISCUSSION

Thermodynamics of Au deposition

Due to different behaviour of various chlorogold complexes, speciation of this metal is an important factor that affects the reduction and electrodeposition mechanisms of gold in aqueous solutions. In addition to temperature, the chloride ion and hydrogen ion concentrations determine the relative concentration of the chlorogold complexes. It is reported that at a low pH (<3), the predominant complex of gold is AuCl_4^- and its hydrolysis will produce an increase in the pH of the solution [22]. Subsequently, chlorogold-hydroxyl complexes will form in the aqueous chloride solution. The chlorogold-hydroxyl complexes are formed as in the following reactions [22, 36]:



In this work, the influence of pH (1, 3, 5 and 7) on the deposition rate and morphology of the metal deposited

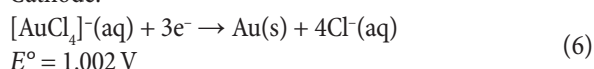
were evaluated using the same initial gold concentration (250 mg L⁻¹).

The most predominant galvanic reaction in the batch reactor can be represented by the following equations:

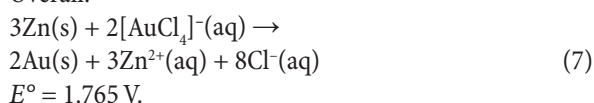
Anode:



Cathode:



Overall:



E° are standard reduction potential values for half reactions in equations (5) and (6). The overall cell potential during the experiment is $1.743 \pm 0.050 \text{ V}$. Thermodynamic parameters were obtained by measuring the overall potential (E) and calculating the cell potential of the system theoretically. Due to the fact that the dominant form of Au at pH 1 and 3 is AuCl_4^{-} [22, 28] the reported calculations are based on the reduction potential of AuCl_4^{-} (E°) at these two pH values. The standard-state Gibbs free energy (ΔG°) was obtained from the E° of the system. The enthalpy (ΔH°) and entropy (ΔS°) were then calculated from the slope and intercept of the van't Hoff plots, k_{rxn} was calculated using Eqs. (8) and (9) from values of E°_{cell} obtained at various temperatures. Eq. (11) was derived from Eqs. (9) and (10) and was plotted at pH 1 and 3 as shown in Fig. 1. The value of ΔG° is $-1.021 \text{ kJ mol}^{-1}$. ΔH° and ΔS° are $-24.56 \text{ kJ mol}^{-1}$ and $0.675 \text{ kJ mol}^{-1}\text{K}^{-1}$ at pH 3 and $-25.24 \text{ kJ mol}^{-1}$, $0.664 \text{ kJ mol}^{-1}\text{K}^{-1}$ at pH 1 and 25°C respectively.

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} \quad (8)$$

$$\Delta G^{\circ} = -RT \ln k_{\text{rxn}}, \quad (9)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}, \quad (10)$$

$$\ln k_{\text{rxn}} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}. \quad (11)$$

From the enthalpy value it is concluded that the reaction is exothermic and hence as temperature increases, the equilibrium constant will decrease. A large negative value of the Gibbs free energy indicates a spontaneous overall reaction in the system.

Dependency of Au deposition on pH

Fig. 2 shows the deposition performance as a function of time at various pH values. It was observed that there is an increase in the rate of electrodeposition with an increase in solution acidity, which may be due to higher concentration of chloride ions. This increase may result from the formation of more stable species of gold complexes at low pH [37]. At a pH of 1 and 3, 100% of gold was deposited within one hour. A model of the concentration-time relationship for a three-dimensional electrode has been reported [38] which is presented in Eq. (12):

$$\ln \left[\frac{C_t}{C_0} \right] = \frac{-V_e k_m A_e}{V_R} t, \quad (12)$$

where C_t is the metal concentration at time t , C_0 is the initial metal concentration, V_e is the volume of cathode, V_R is the total volume of catholyte in the cell, k_m is the mass transport coefficient and A_e is the specific surface area of cathode. The figure of merit is $k_m A_e$ for three-dimensional electrodes. The table shows the $k_m A_e$ values in relation to the constant rate of deposition of gold on the cathode. The mass transport coefficient is calculable because in this study V_e/V_R is constant. The effective electrode area is difficult to determine due to the surface variation occurring during the experiment, therefore the 'volumetric' mass transport coefficient value implies a better understanding of the comparative performance of different applied conditions. The inset of Fig. 2 shows the graph $\ln(C_t/C_0)$

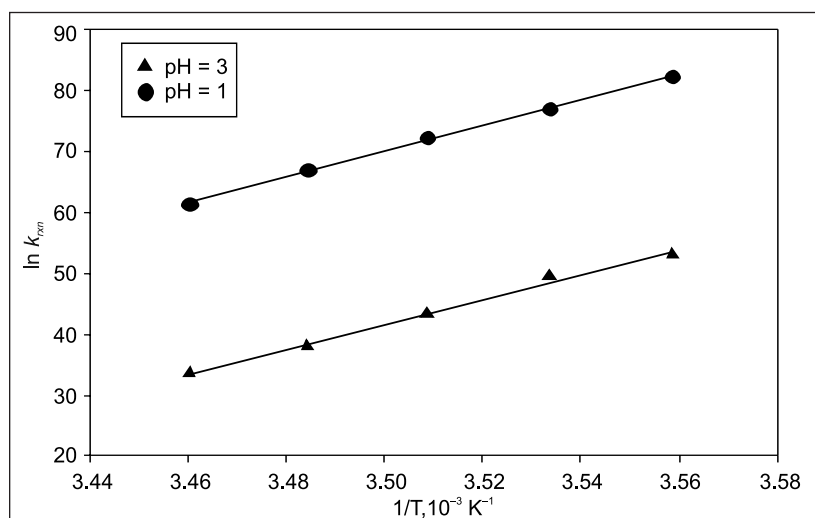
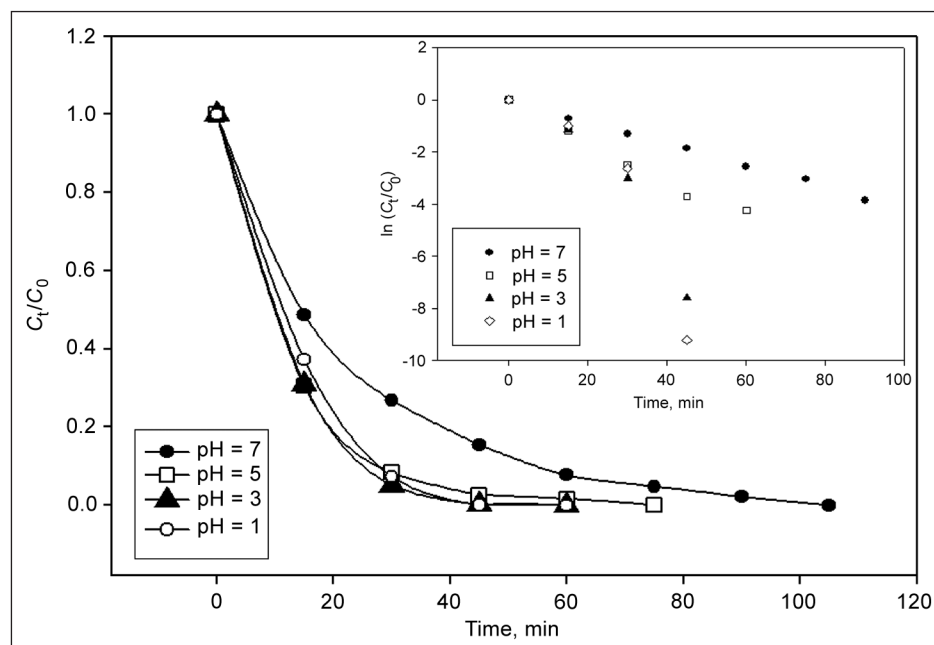


Fig. 1. van't Hoff plot for 250 mg L⁻¹ Au(III) solution at pH 1 and 3

Fig. 2. The deposition performance on RVC cathode from 250 mg L⁻¹ Au(III) at various pH, as a function of time. The inset shows the linearization of normalized (C_t/C_0) plot as a function of time at different pH



against time for the RVC cathode at different pH values. It is shown that the system deviated from undergoing a simple pseudo-first-order reaction for RVC while the R^2 value was low. It is observed that a slight deviation of $\ln(C_t/C_0)$ against time from linearity occurred for RVC because of its high deposition rate. The performance of the system with different pH values was evaluated in terms of $t_{90\%}$. $t_{90\%}$ is the deposition time in which 90% of gold in the catholyte was deposited. This value also implies the deposition rate. In general, it seems that a pH value of less than 3 is more favourable for the electrodeposition of gold in chloride media. The rate of deposition depends directly on the hydrogen ion concentration, so reducing the pH value enhances the deposition efficiency. It is reported elsewhere that increasing the pH makes the AuCl_4^- complex more unstable and some of the chloride ligands are exchanged with OH^- ions [39], which could be responsible for a lower rate of deposition at higher pH levels.

UV studies

To investigate the mechanism of gold deposition from chloride media, UV-Visible spectra of the gold(III) solutions were obtained at various pH values (2, 7 and 11). Fig. 3 shows the predominant gold complex AuCl_4^- bands in acidic media, which are located at 228 and 312 nm. The predominant com-

plex of gold is AuCl_4^- at pH below 2 [22, 40]. Increasing the pH of the solution causes hydrolysis of AuCl_4^- ions to form $[\text{AuCl}_3(\text{OH})]^-$, $[\text{AuCl}_2(\text{OH})_2]^-$, $[\text{AuCl}(\text{OH})_3]^-$, $[\text{Au}(\text{OH})_4]^-$ species and the peak at 312 nm starts to disappear. At higher pH values, there are intermediate forms of gold complexes that contain hydroxyl ligands [27, 36, 37, 39, 41, 42]. Sulfur(IV) was used to study the kinetics of gold(III) complex reduction [43] and it was found that the reduction of gold follows different steps, in which gold produces different reduction states as Au(II) and Au(I). Paclawski and Fitzner showed that gold hydroxyl complexes, which are formed by increasing pH, were not able to be reduced to metallic gold. It is supposed that gold deposition would be more efficient in acidic conditions. However, working at high acidic pH levels (in which the predominant gold complex is AuCl_4^-) needs more considerations with regard to the type of membrane and anode.

pH effect on zinc anode

The chemical and physical behaviour of zinc metal has been discussed elsewhere [44, 45]. In particular, its corrosion and passivation reactions under different conditions of the potential and pH have also been reported along with Eh/pH diagrams [46, 47]. Zinc solubility depends on the temperature and pH of the solution. Various zinc complexes are formed

Table. Cell performance for the gold deposition from 250 mg L⁻¹ Au(III) solution on RVC cathode at various pH values

Cathode type	pH value	Time in which 90% of gold was electrodeposited, min	R^2	Slope, min ⁻¹	$k_m A_e^*$, s ⁻¹
RVC (80ppi)	1 ± 0.02	<30	0.8123	0.1639	6.8 × 10 ⁻²
	3 ± 0.02	<30	0.8631	0.1405	5.9 × 10 ⁻²
	5 ± 0.02	~30	0.9588	0.0726	3.0 × 10 ⁻²
	7 ± 0.02	~60	0.9834	0.0458	1.9 × 10 ⁻²

* $k_m A_e^*$ is volumetric mass transport coefficient for a three-dimensional electrode.

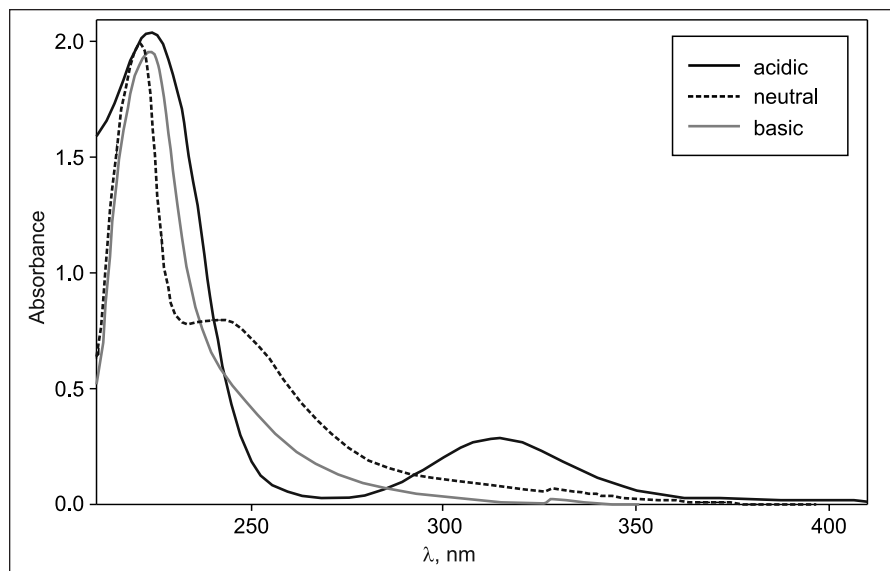
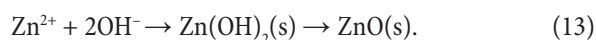
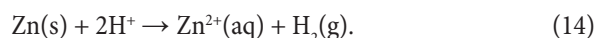


Fig. 3. UV-Visible spectra of 10 mg L^{-1} Au(III) solutions obtained at different pH (2, 7 and 11)

under different conditions and in some cases zinc would be passivated by formation of an insoluble film. Since zinc is used as a sacrificial anode in a galvanic cell, this film may prevent electrons transferring from zinc to the cathode. Acidic pH aids in the corrosion and dissolution of Zn. In chloride media at a pH higher than 3, zinc exists as zinc-chloro complexes, and depending on the chloride ion concentration, acidic, neutral and basic forms of zinc complexes are expected [48]. In solutions with pH less than 7, ZnCl_2 is hydrolyzed and forms Zn(OH)_2 , which can then dehydrate to form the anhydrous oxide ZnO (a solid film), according to the following reaction [49]:



The most common reaction of zinc dissolution in dilute acidic media is presented below. In solutions with acidic pH values, zinc reacts with H^+ ions and releases hydrogen [50]:



This hydrogen evolution increases with a decrease in pH and since zinc is used as a sacrificial anode, it may be involved in two parallel oxidation reactions that result in a higher loss of zinc metal. Due to zinc passivation, lower rates of dissolution and corrosion will occur at near neutral and slightly alkaline pH values. The level of dissolution and corrosion increases in acidic and strongly alkaline pH. Moreover, some of the electrolytes enhance the zinc corrosion reaction rate [49]. Phosphate solution was used to adjust the pH values to the desired level. At acidic pH values, the cathodic reaction of hydrogen evolution takes place on the anode surface and also the formation of the zinc-phosphate film proceeds slowly [44, 49]. This occurrence is enhanced by increasing the pH, especially at pH 3–12. At the pH levels below 3, this film is completely soluble, whereas at higher pH levels, it is converted to zinc hydroxide, which then

is decomposed to ZnO and is dissolved at higher pH levels as zincate ion. At a neutral pH, in the initial steps of the reaction the anode surface is free of the passivating material and the rate of deposition is fast. As the passivating layer forms, the deposition rate decreases gradually. It is concluded that, in addition to the film of phosphate complexes developing, surface passivation will occur due to Zn(OH)_2 and ZnO formation at elevated pH values, which reduces the conductivity of the anode [47]. Even though the highest deposition rate is at pH 1, it will be at the expense of the zinc anode. Therefore pH 3 is favoured in terms of zinc consumption (lower than pH 3) and prevention of zinc passivation (pH 5–7).

Morphology of gold deposits

SEM studies

After gold deposition from 250 mg L^{-1} Au(III) solution was carried out at various pH levels on RVC (after 1 hour of deposition), the cathode surfaces were analysed using SEM as shown in Figs. 4(a–d). The deposited gold was granular in the shape at pH 1, Fig. 4(a). By increasing the pH from pH 1 to pH 7, the spherical grains were attached together, aggregated and tended to form the sponge shaped gold at pH 7, Fig. 4(d). The deposited gold grains on the RVC at pH 1 were small and homogeneous. This result could be attributed to the fast rate gold reduction at more acidic pH levels, which provides a more suitable potential for the nucleation of gold particles rather than particle growth. Moreover, RVC, as a porous glassy carbon [32], has a smooth surface and purer carbon material. As a result, RVC could offer more opportunities for gold ions to be deposited.

XRD and EDX Studies

Metallic gold formation was confirmed by XRD and SEM-EDX analyses. The deposited gold was obtained from 250 mg L^{-1} Au(III) solution on RVC for 60 minutes at different pH values. In all cases it was established that the deposition

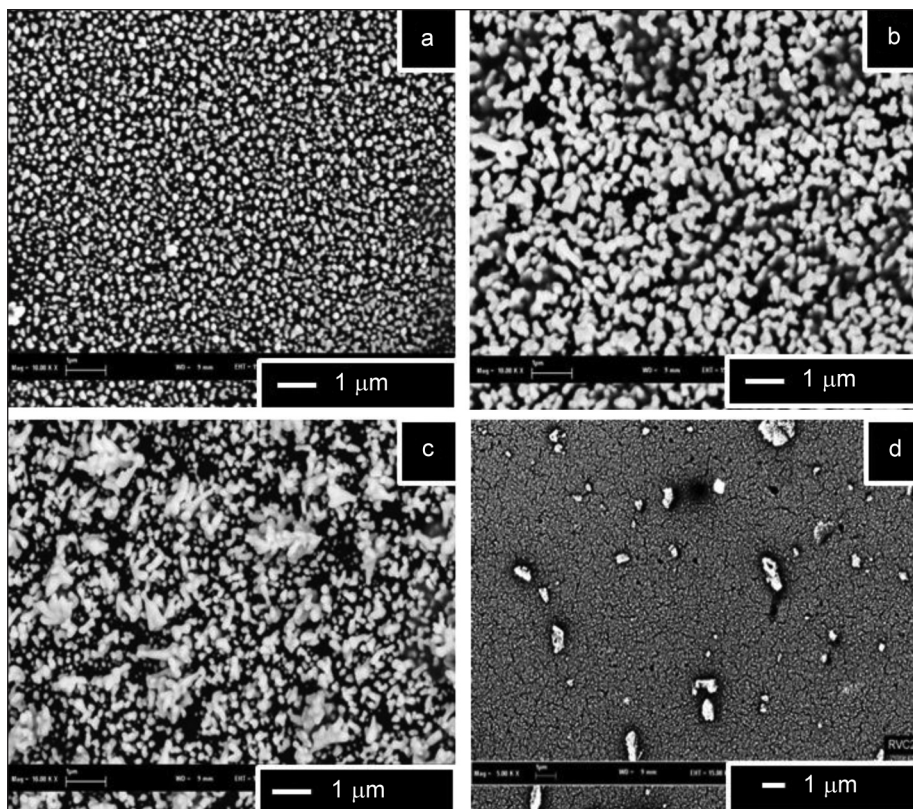


Fig. 4. (a–d) SEM images of gold electrodeposition onto RVC electrode at different pH (1, 3, 5 and 7)

of metallic gold took place. The XRD pattern in Fig. 5, which was obtained at pH 7, shows that the 2θ values of the peaks at 38.2, 44.4, 64.6, 77.5 and 81.7° match those of metallic gold peaks, which shows the formation of elemental gold on the cathode surface during the deposition process [51]. The calculated mean crystallite size was 73.8 nm based on the XRD data. The EDX in the inset of Fig. 5 also shows deposition of

gold. From the crystallographic information of XRD it is confirmed that the gold crystal system was cubic.

Electrooxidation of ethanol on AuNPs/RVC in alkaline medium

Fig. 6 shows the cyclic voltammograms of AuNPs/RVC substrate in 2.00×10^{-1} M NaOH in the absence and presence of

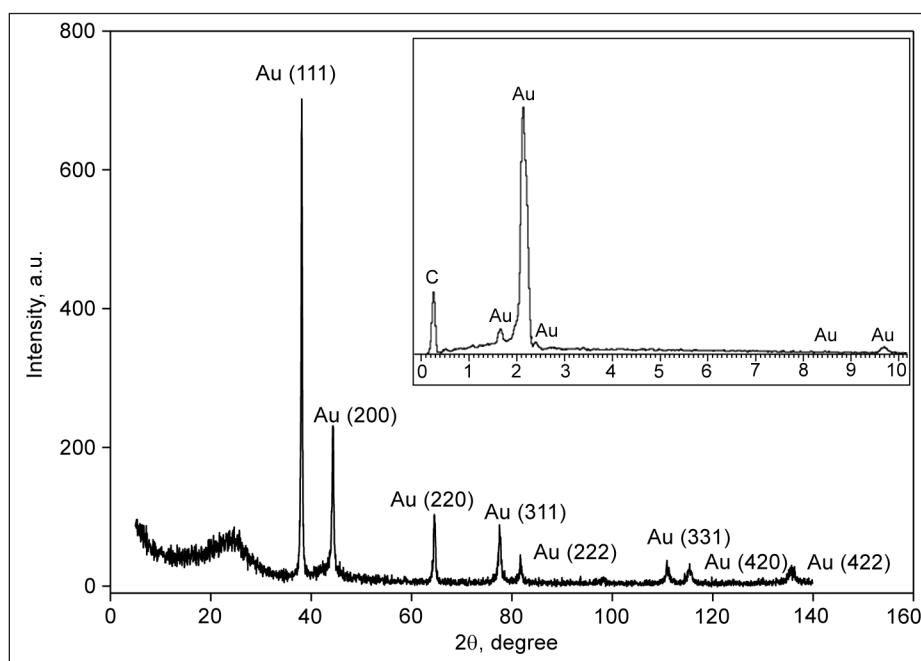


Fig. 5. X-ray diffraction pattern of metallic gold. The inset depicts the EDX of the cathode substrate after gold deposition process

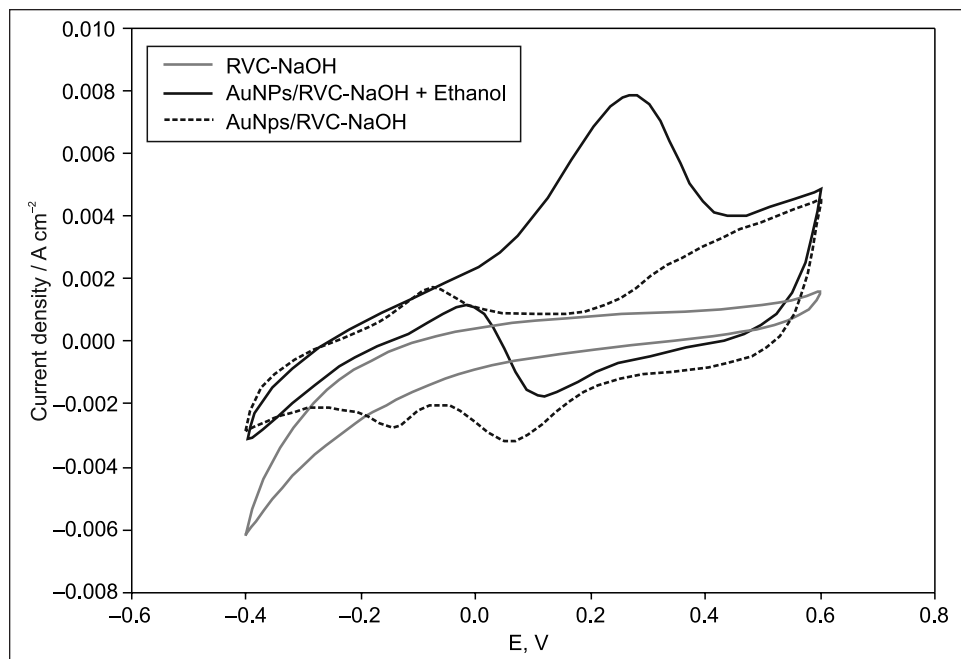


Fig. 6. The cyclic voltammograms of bare RVC and AuNPs/RVC substrate in 2.00×10^{-1} M NaOH in the absence and presence of ethanol (2.00×10^{-1} M) in the potential range of -400 mV to 800 mV at a scan rate of 100 mV s⁻¹

ethanol (2.00×10^{-1} M) in the potential range of -400 mV to 800 mV at a scan rate of 100 mV s⁻¹. As can be seen in the Figure, activity of RVC is negligible in the supporting electrolyte (NaOH). It is supposed that two oxidation peaks (ca. -0.1 V and onset ca. 0.2 V) are due to desorption of hydrogen and oxidation of gold atoms. Two reduction peaks (ca. 0.06 V and -0.15 V) are due to the reduction of gold surface oxides and hydrogen adsorption. The AuNPs/RVC electrode is highly active in the alkaline solution containing ethanol. The oxidation peak in the positive-going (forward) sweep is assigned to the oxidation of ethanol while reduction and reoxidation peaks in the negative-going (backward) sweep are ascribed to

reduction of gold surface oxides (which were oxidized during the forward sweep) and oxidation of species that have been generated during the forward sweep.

The electrode prepared after a deposition time of 240 s was applied for the stability analysis. At a scan rate of 100 mV s⁻¹ 50 cycles were performed. The anodic peak currents of ethanol oxidation were stable even after 50 cycles which reveals that the AuNPs/RVC electrode is steady under the applied settings as presented in Fig. 7. The inset of Fig. 7 shows the 5th cycle of the electrooxidation of ethanol on the AuNPs/RVC catalysts in the presence of 2.00×10^{-1} M ethanol and NaOH at a scan rate of 100 mV s⁻¹.

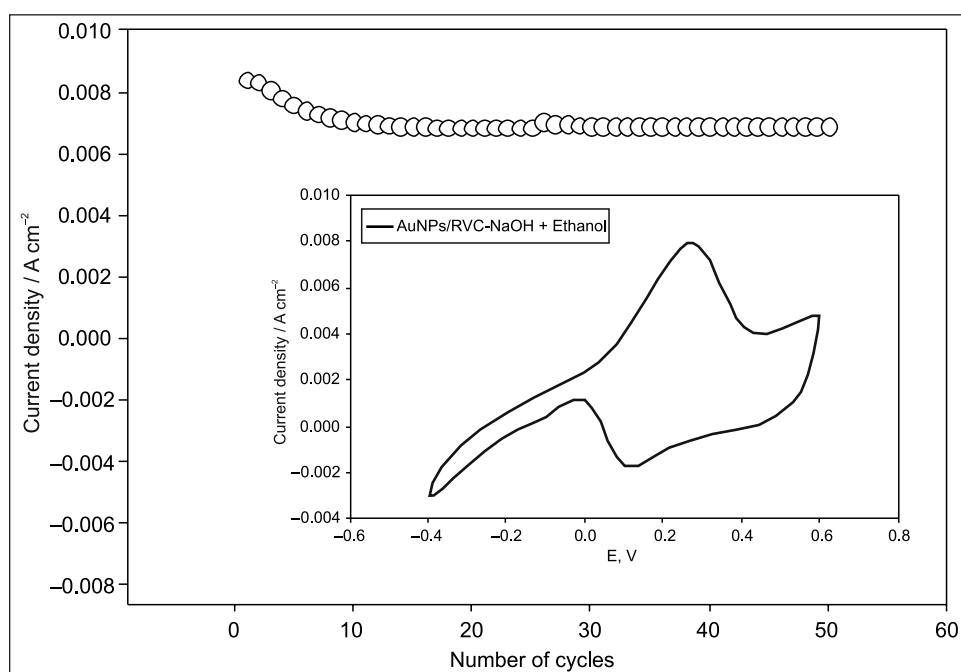


Fig. 7. Test of electrode stability after 50 cycles. Inset: The cyclic voltammogram of AuNPs/RVC in the presence of 2.00×10^{-1} M ethanol and NaOH at a scan rate of 100 mV s⁻¹

The electrocatalysis of ethanol on bare gold electrode, adatoms modified gold electrode, some conducting polymers as substrate and Pt and PtRu electrodes have been reported [1, 52, 53]. Compared to these studies, our reported work offers a simple, clean and cost effective method for the preparation of AuNPs catalysts. The calculated current density is $\sim 8 \text{ mA cm}^{-2}$ which shows high catalytic activity of the as-prepared AuNPs/RVC in this study in comparison with the reported ones (1.0 M ethanol in 5.0×10^{-1} M NaOH) at different Au-CP nanocomposite film: (a) Au-PANI nanocomposite film, $\sim 3.2 \text{ mA cm}^{-2}$; (b) Au-PPY nanocomposite film, $\sim 2 \text{ mA cm}^{-2}$; (c) Au-PTP nanocomposite film, $\sim 1.7 \text{ mA cm}^{-2}$ and (d) Au-PEDOT nanocomposite film, $\sim 3 \text{ mA cm}^{-2}$ [1] or in the range of μA for Pt and PtRu electrodes [53].

CONCLUSIONS

When RVC is used as the cathode material, the deposition rate is similar at pH 1 and 3. However, when considering the deposition rate, anode usage and cathode material, the best condition is pH 3. The electrogenerative process provides an alternative method for gold deposition with a clean and environmental friendly process to electrodeposit this precious metal. Electrochemical investigations implied that AuNPs/RVC catalyst indicated notable electrocatalytic activity for the oxidation of ethanol. Further studies are underway to enhance the catalytic activity of this catalyst and improve its performance.

ACKNOWLEDGMENTS

This study was supported by the Malaysian Ministry of Higher Education under the Fundamental Research Grant Scheme (FRGS). F. S. K. would like to express her gratitude to Universiti Sains Malaysia (USM) for a postgraduate assistantship.

Received 18 May 2012

Accepted 11 September 2012

References

- R. K. Pandey, V. Lakshminarayanan, *Appl. Catal., B*, **125**, 271 (2012).
- P. Alexandridis, *Chem. Eng. Technol.*, **34**, 15 (2011).
- M. Etesami, N. Mohamed, *Int. J. Electrochem. Sci.*, **6**, 4676 (2011).
- M. Etesami, N. Mohamed, *Sci. China Ser. B*, **55**, 247 (2012).
- A. Mirescu, U. Prüße, *Catal. Commun.*, **7**, 11 (2006).
- K. Tomishige, T. Miyazawa, T. Kimura, K. Kunimori, *Catal. Commun.*, **6**, 37 (2005).
- H. Kominami, H. Sugahara, K. Hashimoto, *Catal. Commun.*, **11**, 426 (2010).
- G. Tremiliosi-Filho, E. R. Gonzalez, A. J. Motheo, E. M. Belgsir, J. M. Léger, C. Lamy, *J. Electroanal. Chem.*, **444**, 31 (1998).
- S. Zoladek, I. A. Rutkowska, P. Kulesza, *J. Appl. Surf. Sci.*, **257**, 8205 (2011).
- M. J. Lippits, B. E. Nieuwenhuys, *J. Catal.*, **274**, 142 (2010).
- M. Pasta, F. La Mantia, Y. Cui, *Electrochim. Acta*, **55**, 5561 (2010).
- S. N. Raicheva, S. V. Kalcheva, M. V. Christov, E. I. Sokolova, *J. Electroanal. Chem. Interfac.*, **55**, 213 (1974).
- T. Nelson, *Bioelectrochemistry*, **76**, 195 (2009).
- L. S. Pangum, R. E. Browner, *Miner. Eng.*, **9**, 547 (1996).
- S. Kulandaisamy, J. Rethinaraj, P. Adaikkalam, G. Srinivasan, M. Raghavan, *JOM*, **55**, 35 (2003).
- S. Sobri, S. Roy, *J. Electrochem. Soc.*, **152**, C593 (2005).
- C. Zur, M. Ariel, *J. Appl. Electrochem.*, **12**, 231 (1982).
- C. Zur, M. Ariel, *J. Appl. Electrochem.*, **11**, 639 (1981).
- R. Qu, C. Sun, M. Wang, et al., *Hydrometallurgy*, **100**, 65 (2009).
- G. Tsekouras, S. F. Ralph, W. E. Price, G. G. Wallace, *Fiber. Polym.*, **5**, 1 (2004).
- Z. Wang, D. Chen, L. Chen, *Miner. Eng.*, **20**, 581 (2007).
- T. Ogata, Y. Nakano, *Water Res.*, **39**, 4281 (2005).
- F. Salehi Karoonian, M. Etesami, N. Mohamed, *Int. J. Electrochem. Sci.*, **7**, 3059 (2012).
- F. S. Karoonian, M. Etesami, M. A. Hasnat, N. Mohamed, *Catal. Commun.*, **21**, 14 (2012).
- C. H. Gammons, Y. Yu, A. E. Williams-Jones, *Geochim. Cosmochim. Acta*, **61**, 1971 (1997).
- J. A. Tossell, *Geochim. Cosmochim. Acta*, **60**, 17 (1996).
- S. Wang, K. Qian, X. Bi, W. Huang, *J. Phys. Chem. C*, **113**, 6505 (2009).
- I. Mironov, E. Makotchenko, *J. Solution Chem.*, **38**, 725 (2009).
- W. Patungwasa, J. H. Hodak, *Mater. Chem. Phys.*, **108**, 45 (2008).
- P. T. Davies, B. Vincent, *Colloids Surf. Physicochem. Eng. Aspects*, **354**, 99 (2010).
- R. S. Juang, S. W. Wang, *Water Res.*, **34**, 3795 (2000).
- J. M. Friedrich, C. Ponce-de-León, G. W. Reade, F. C. Walsh, *J. Electroanal. Chem.*, **561**, 203 (2004).
- T. Cheng, E. Gyenge, *J. Appl. Electrochem.*, **38**, 51 (2008).
- Z. Jiang, Z.-J. Jiang, Y. Meng, *Appl. Surf. Sci.*, **257**, 2923 (2011).
- Y. Sun, L. Sun, F. Xu, et al., *Appl. Surf. Sci.*, **255**, 6814 (2009).
- P. J. Murphy, G. Stevens, M. S. LaGrange, *Geochim. Cosmochim. Acta*, **64**, 479 (2000).
- B. Chatterjee, *Mater. Chem. Phys.*, **45**, 27 (1996).
- R. C. Widner, M. F. B. Sousa, R. Bertazzoli, *J. Appl. Electrochem.*, **28**, 201 (1997).
- A. Usher, D. C. McPhail, J. Brugger, *Geochim. Cosmochim. Acta*, **73**, 3359 (2009).
- K. S. Nam, B. H. Jung, J. W. An, T. J. Ha, T. Tran, M. J. Kim, *Int. J. Miner. Process.*, **86**, 131 (2008).
- G. V. K. Puvvada, D. S. R. Murthy, *Hydrometallurgy*, **58**, 185 (2000).
- M. Laatikainen, E. Paatero, *Hydrometallurgy*, **79**, 154 (2005).
- K. Paclawski, K. Fitzner, *Metall. Mater. Trans. B*, **35**, 1071 (2004).

44. U. R. Evans, *The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications*, E. Arnold, London (1960).
45. H. H. Uhlig, R. W. Revie, *Corrosion and Corrosion Control*, Wiley-Interscience, New York (1985).
46. N. D. Tomashov, G. P. Chernova, *Passivity and Protection of Metals Against Corrosion*, Plenum Press, New York (1967).
47. K. R. Trethewey, J. Chamberlain, *Corrosion: For Students of Science and Engineering*, Longman Scientific & Technical, Burnt Mill, UK (1988).
48. A. Borowiak-Resterna, H. Chlebowska, M. Giezek, *Hydrometallurgy*, **103**, 158 (2010).
49. X. G. Zhang, *Corrosion and Electrochemistry of Zinc*, Plenum Press, New York (1996).
50. A. E.-K. B. Mostafa, S. M. Abdel-Wahaab, E.-S. M. Mabrouk, *Surf. Coat. Technol.*, **27**, 317 (1986).
51. D. Parajuli, H. Kawakita, K. Inoue, M. Funaoka, *Ind. Eng. Chem. Res.*, **45**, 6405 (2006).
52. Z. Dursun, Å. Ulubay KarabiberoÇşlu, B. Gelmez, A. BaÅYaran, *Turk. J. Chem.*, **35**, 349 (2011).
53. M. F. Silva, B. C. Batista, E. Boscheto, H. Varela, G. A. Camara, *J. Braz. Chem. Soc.*, **23**, 831 (2012).

Fatemeh Salehi Karoonian, Mohammad Etesami,
Norita Mohamed

NESUDĖTINGAS AUKSO NANODALELIŲ ELEKTRO- NUSODINIMAS ANT TINKLINĖS STIKLO ANGLIES ELEKTRODO ESANT SKIRTINGOMS TIRPALO PH VERTĖMS ETANOLIO ELEKTROOKSIDAVIMUI

S a n t r a u k a

Buvo tiriamas aukso nusodinimas ant tinklinės stiklo anglies naudojant tirpalą, turintį $AuCl_4^-$ jonų, ir natrio chloride esant skirtingoms tirpalo pH vertėms. Nustatytos optimalios sąlygos gauti tinkamoms aukso nanodalelėms. Šios nanodalelės, nusodintos ant elektrodo paviršiaus, panaudotos etanolio elektrokatalizei.