Electrodeposition of Au on Reticulated Vitreous Carbon From Chloride Media by an Electrogenerative Process

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This study has been initiated to investigate the electrodeposition of gold by an electrogenerative process in a batch reactor containing solutions of $HAuCl_4$ salt and sodium chloride as a supporting electrolyte. In the process, porous graphite (PG) and 80 ppi reticulated vitreous carbon (RVC) as three - dimensional cathodes, stainless steel and copper sheets as two-dimensional cathode materials and zinc as an anode were used. With RVC as the cathode, more than 99% of gold was deposited from a 500 mg L^{-1} Au(III) in 0.2 M NaCl and 0.4 M NaH_2PO_4 solution at pH 7 after 90 min operation of the reactor. The effect of varying deposition times on the morphology of the gold deposits on different cathode materials was also investigated.

1. INTRODUCTION

The exclusive physical and chemical properties of gold have made it a key metal in the electronics industry. The recovery of gold has attracted much attention due to increasing industrial demands and limited resources. The conventional method to leach and recover gold is to use cyanide solutions, but owing to its toxicity, many efforts have been carried out to replace the conventional gold-cyanidation solutions with suitable alternative lixiviates such as thiourea [1], thiosulphate [2-4], sulfite, thiocyanate [5, 6], ascorbic acid, mixed baths [7] and chloride media [8-15]. These efforts have focused on two main aspects, i.e. gold leaching from ores and recovery from leachate solutions. A series of alternative lixiviant systems for gold leaching from ores and scraps [5, 11, 13, 16] and gold recovery [17-20] have been reported. Several methods have been used for the recovery of gold, such as electrogenerative processes [21, 22], cementation [6], use of ion exchange resins [23] and biosorption. In metal recycling we are mostly dealing with dilute solutions with low amounts of target metal, hence

there are many factors that should be considered toward controlling the side reactions, kinetics and thermodynamics of the system along with the operating cost. Regarding the control of these factors, the researchers may face many experimental limitations. All systems mentioned above involve several additional stages such as pre-concentration, eliminating side reactions and using more costly materials. The solution of these problems calls for a recommended and promising method which has more benefits in terms of reducing effluents and side reactions. An electrogenerative process or system is a suitable solution to overcome these difficulties, which unlike electrolytic methods, do not need any external power supply.

Electrogenerative systems would eliminate the external power resource and is applicable in providing advantages with respect to ease of operation and scale up system as well as its operating cost. To the best of our knowledge there is no report on electrogenerative gold recovery from chloride media. The present paper focuses on recovering of gold from non-cyanide media by using an electrogenerative process, monitoring the morphological changes of gold nanoparticles electrodeposited on RVC and PG and exploring the possibilities of electrogenerative deposition of nanoparticles on microporous matrices. RVC has a low density, low thermal expansion, high corrosion resistance and high electrical conductivity. RVC is an open-pore foam material of honeycomb structure composed solely of vitreous carbon [24]. The leaching of gold with various lixiviants has been used to extract gold from ores.

The reason for choosing $HAuCl_4$ salt as the source of gold ions in this study is that during the leaching process, based on the dissolution of the gold in chloride media, the predominant species of $AuCl_4^-$ is resulted [9, 13, 15]. Hence this electrogenerative approach could also be applicable to recover gold from industrial liquors. In order to recover gold from this type of leachate solution, the condition was simulated by using commercial $HAuCl_4$ salts in this work. The pH of solution was adjusted to a neutral pH to minimize the side reactions in the system involving components such as plastic and the polymeric membrane.

2. MATERIALS AND METHODS

2.1. Materials

Hydrogen tetrachloroaurate(III) trihydrate, $HAuCl_4.3H_2O$ (> 99.9% purity) was obtained from Sigma-Aldrich and sodium chloride, sodium di-hydrogen phosphate and other chemicals used were of analytical grade. The anion exchange membranes used were Neosepta® AM-01 (Tokuyama Corp.) and Mega RALEX AMH-PAD 1000×420 and the cation exchange membranes were Neosepta® CM-01 (Tokuyama Corp.) and Mega RALEX CM-PAD 1000 ×420. The anode was pure zinc (99% purity) of dimensions 2.5 cm × 5 cm × 0.05 cm. The cathode materials used for gold recovery were PG sheet (National Electrical Carbon Products, Inc., 2.5 cm × 4 cm × 0.5 cm), RVC 80 pores per inch (ppi) (The Electrosynthesis Co., 2 cm × 4 cm × 0.5 cm), stainless steel and copper plates (2.5 cm × 4 cm × 0.05 cm).

2.2. Apparatus and procedure

2.2.1. Gold deposition studies

The electrogenerative deposition was carried out in a batch cell made of Plexiglas. The cell consisted of two electrolyte compartments of dimensions 5.5 cm x 5.5 cm x 8.0 cm separated by an ion exchange membrane. The schematic diagram of the batch cell is presented in Fig. 1.
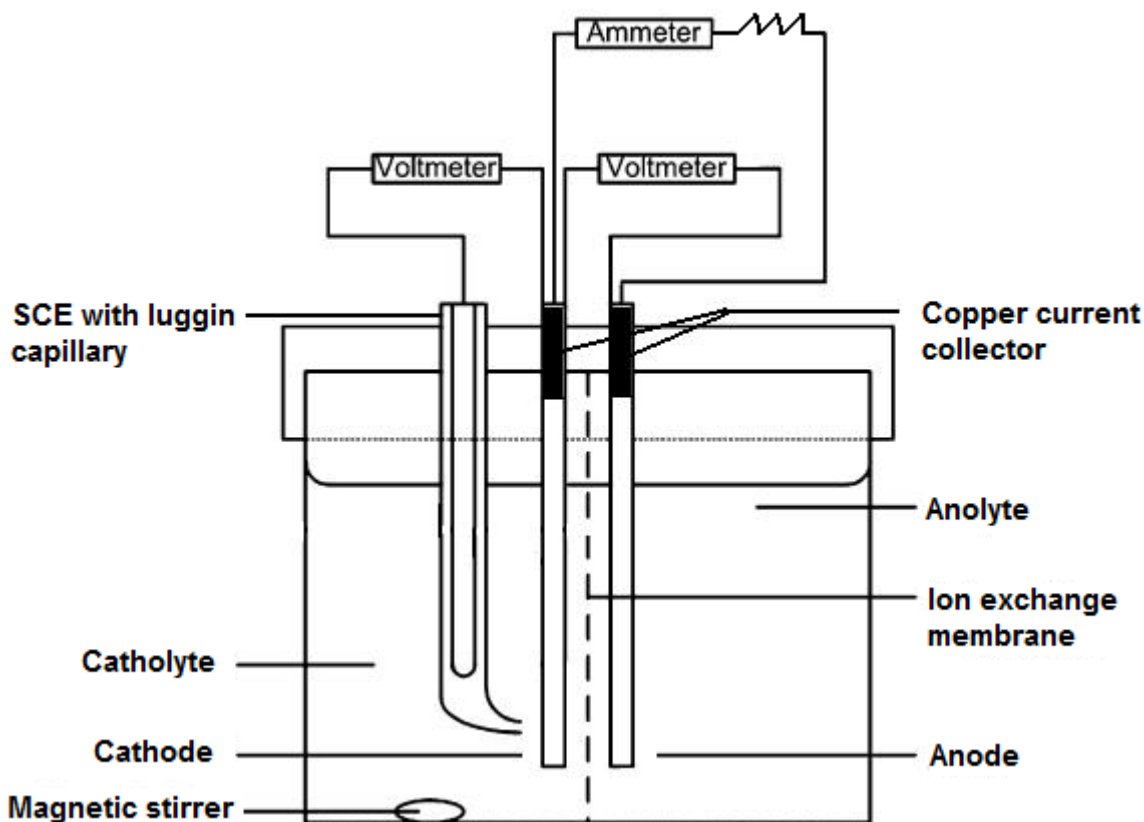
Figure 1. Schematic diagram of batch cell and its electrical circuit.

The cell components were held together with 9 nuts and bolts. The electrodes were connected to copper sheets, which were used as current collectors. Parafilm was wrapped around the junction of the cathode and the current collector in order to prevent the gold being deposited on the surface of the current collector. An external conducting wire was connected to the current collectors to complete the circuit. To monitor the potential of the cathode a saturated calomel electrode (SCE) with a Luggin capillary was used as a reference electrode.

Gold deposition studies onto the cathode were carried out in a catholyte solution containing varying concentrations of Au(III) and 0.2 M NaCl. The anolyte solution is 0.1 M NaCl. Sodium dihydrogen phosphate (0.4 M) which acts as a buffer was used in both the catholyte and anolyte solutions. Table 1 shows the details of the experimental conditions used. All of the solutions were prepared with deionised water 18 MΩ.cm. All the experiments were performed at room temperature

(~25 ^{o}C). The pH was adjusted to 7 by using dilute NaOH or HCl solutions. One hundred millilitres of solution was used in each compartment. The catholyte was stirred continuously with a constant speed during all experiments.

Table 1. Details of experimental conditions

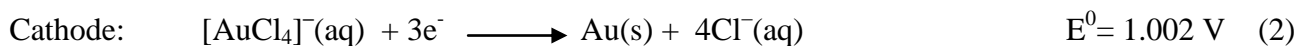| Anode compartment		Cathode compartment	
Anolyte	100 ml of 0.4 M NaH$_2$PO$_4$ 0.1 M NaCl	Catholyte	100 ml of 0.4 M NaH$_2$PO$_4$ solution (50, 125, 250 and 500) mg L^{-1} Au(III) 0.2 M NaCl
Anode	Zinc foil 99%	Cathode	RVC 80 ppi, porous graphite(PG), Copper plate, stainless steel plate

The determination of Au(III) concentration in the catholyte solution was carried out periodically using an atomic absorption spectrometer (Perkin Elmer AAnalyst 200) to monitor the performance of the system in terms of percentage of gold recovered. As a test of reproducibility, each experiment was performed three times. The surface morphology of the gold deposits was visualized by scanning electron microscopy (SEM) (Leo Supra 50 VP) and characterized using X-ray diffraction (XRD) and energy-dispersive X-ray analysing system (EDX).

2.2.2. Cathodic polarization studies

In the cathodic polarization study, three replicate polarization curves were recorded to ensure reproducibility. The system was initially loaded with maximum resistance. After the initial open circuit cell voltage was read, the resistance was gradually decreased by adjusting the variable resistance of a decade resistance box (model 1051, Time Electronic Ltd.) until the cell is short-circuited. The cell was allowed to equilibrate for 1 min after each change in resistance after which the current and cathode potential vs. SCE were recorded. The cathode potential was plotted vs. current densities, which were calculated based on the geometric area of the cathode in contact with the catholyte.

3. RESULTS AND DISCUSSION

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

Anode: $\quad$ Zn^{2+}(aq) + 2e$^-$ $\longrightarrow$ Zn(s) $\qquad\qquad$ E^0= - 0.763 V (1)

Cathode: $\quad$ [AuCl$_4$]$^-$(aq) + 3e$^-$ $\longrightarrow$ Au(s) + 4Cl$^-$(aq) $\qquad$ E^0= 1.002 V (2)

Overall: $\quad$ 3Zn(s) + 2[AuCl$_4$]$^-$(aq) $\longrightarrow$ 2Au(s) + 3Zn^{2+}(aq) + 8Cl$^-$(aq) $\quad$ E^0= 1.765 V (3)

E^0 are standard reduction potential values for half reactions, Eqs. (1) and (2). The overall cell potential during the experiment (1.743±0.050 V), closely approximated the overall positive cell potential given in Eq. (3) indicating that the reaction was spontaneous and the cell electromotive force can provide the driving potential itself.

3.1. Study on the various parameters

The effects on the recovery of gold from chloride media were studied with respect to the following parameters: cathode material, initial Au(III) concentration, supporting electrolyte concentration and membrane properties.

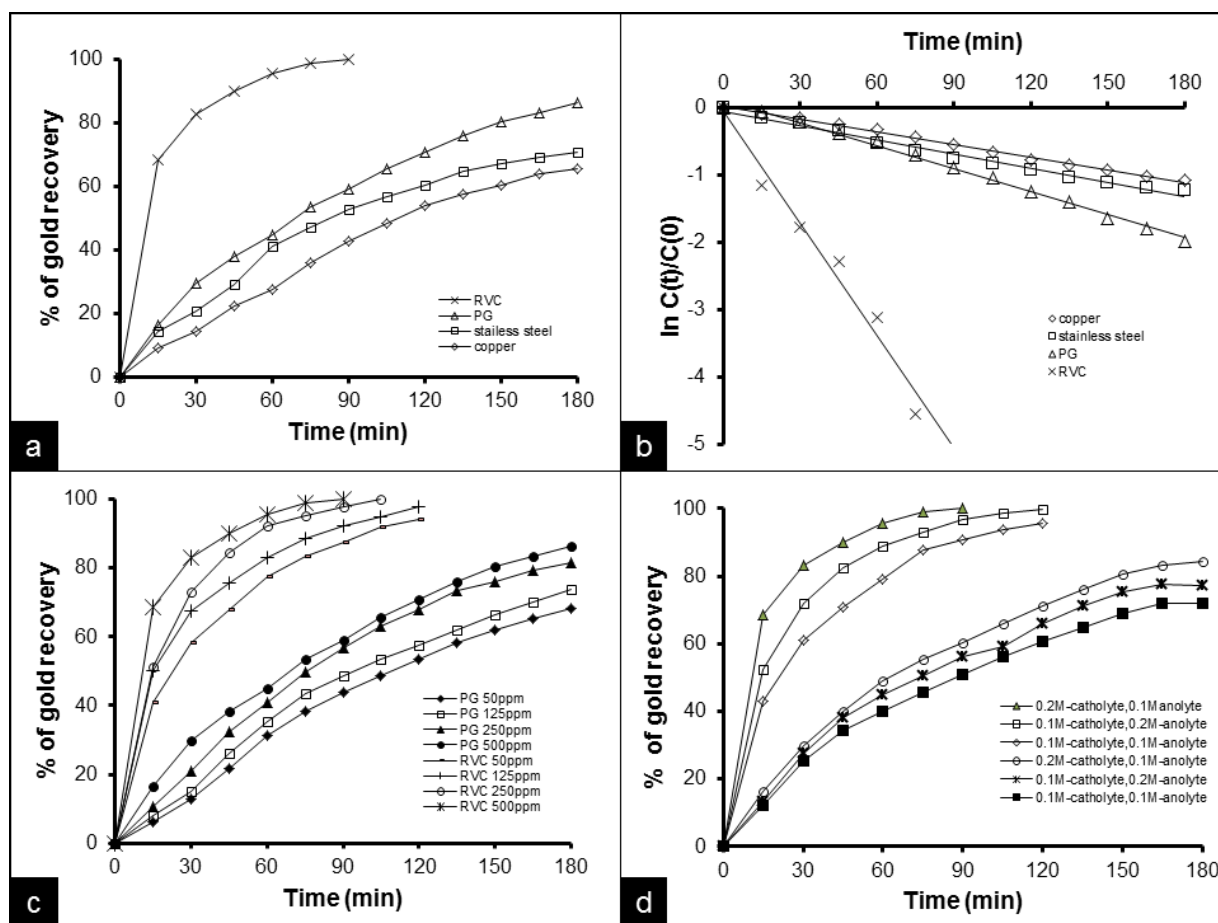### 3.1.1. Effect of cathode material

Figure 2. (a) Percentage of gold recovery vs. time with different cathode types from 500 mg L^{-1} of gold solution within 3 h of experiment; (b) Linearization of normalized gold 500 mg L^{-1} concentration, as a function of time with different cathode types; (c) Effect of initial gold concentration on recovery of gold from chloride media; (d) Effect of supporting electrolyte concentration on the recovery of gold vs. time.

In order to study the effect on recovery of gold from chloride media with various cathode materials, a series of experiments were conducted by short-circuiting the electrogenerative cell. At the start of each experiment, the pH of the catholyte and anolyte solutions was adjusted to 7.

To prevent any increase in pH due to the hydrogen evolution reaction, the pH was readjusted to 7 by adding dilute HCl or NaOH solutions during the experiments. The influence of cathode materials on the cell performance is depicted in Fig. 2. Fig. 2(a) shows the percentage of gold recovery vs. time from 500 mg L^{-1} of Au(III) solution by using different cathode types within 3 h of experiment. It is observed that, RVC can recover gold faster than the other types of cathodes in this study. In order to compare the cathode performance, the percent of recovery after 90 min using different cathodes is presented in Table 2.

Table 2. Cell performance for the gold recovery from 500 mg L^{-1} Au(III) solution with different cathode materials.

Cathode type	R^2	Slope (min^{-1})	k_mA_e[a] or k_mA_s[b] (s^{-1})	% of gold recovery after 90 min	Open circuit potential vs. SCE (V)	Current density at -0.3 V vs. SCE (mA cm^{-2})	Maximum current density (mA cm^{-2})
RVC	0.974	0.0556	0.023	> 99	0.428	3.78	4.396
PG	0.997	0.0114	0.005	59	0.488	0.66	1.009
Stainless steel	0.996	0.0071	1.18×10^{-4}	53	0.480	~0.4	1.775
Copper	0.995	0.0066	1.10×10^{-4}	43	-0.077	0.72	1.518

[a] k_mA_e is volumetric mass transport coefficient used for a three-dimensional electrode.
[b] k_mA_s is volumetric mass transport coefficient used for a two-dimensional electrode.

As it is shown, the percentage of deposited gold is 59% for PG, 53% for stainless steel, 43% for copper and > 99% for RVC. Three-dimensional cathode materials can provide an efficient and low-cost process for metal treatment and recovery from dilute solutions [24]. Fig. 2(b) shows the linearization of normalized concentration of gold as a function of time with different cathodes.

Trinidad et al. [25] reported a model of concentration with respect to time for two-dimensional electrodes, which is expressed in Eq. (4):

$$\ln\left[\frac{C_t}{C_0}\right] = \frac{-k_mA}{V_R}t \tag{4}$$

The same relationship for three-dimensional electrodes is expressed in Eq. (5) [26]:

$$\ln\left[\frac{C_t}{C_0}\right] = \frac{-V_ek_mA_e}{V_R}t \tag{5}$$

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, A is the effective surface area and A_e is the specific surface area of cathode. Due to the surface

variations that take place during the recovery time, the 'volumetric' mass transport coefficient value would be a better definition to a clear understanding of system performance under different conditions. The figures of merit are k_mA_s for two-dimensional electrode systems and k_mA_e for three-dimensional electrode systems, where A_s is the active electrode area per unit reactor volume which can be expressed by Eq. electrode area per unit reactor volume which can be expressed by Eq. (6) [27]:

$$A_s = \frac{A}{V_R} \qquad\qquad (6)$$

The k_mA_e and k_mA_s are the figures of merit for three-dimensional and two-dimensional systems, respectively. Their values are given with slope values representing the rate constant for recovery of gold on the cathode (Table 2).

It is possible to calculate the mass transport coefficient considering that V_e/V_R is constant for the cell configuration used in this study and the approximate electrode areas can be taken from the RVC manufacturer's literature. Fig. 2(b) shows the graph $\ln(C_t/C_0)$ against time for the four types of electrodes.

The deviation of data points from the trend lines for RVC, shows large changes in logarithms of the concentrations over short periods of time. It could be due to the high surface area of this electrode which has provided more available active sites for gold deposition during the experimental time. It is shown that the system with RVC deviated from undergoing a simple pseudo-first order reaction with lower R^2 values obtained. The plot exhibits best fit lines with linear correlation coefficients of 0.99 and above for the other cathode materials. However, a slight deviation of $\ln(C_t/C_0)$ against time from linearity occurs for RVC because of its higher deposition rate, compared to other cathode types.

3.1.2. Effect of initial Au(III) concentration

The performance of the system was further evaluated as a function of Au(III) concentration, using both types of electrodes, PG and RVC.

One hundred milliliters of solutions with 50, 125, 250 and 500 mg L^{-1} Au(III) were used in the catholyte compartment. Fig. 2(c) shows that as the concentration was increased, the percentage for gold recovered increased over a shorter period of time.

It could be attributed to enhancement in the gold concentration gradient between the solution and cathode surface during the recovery process [6]. It should be noted that another key parameter is the size of the cathodes which plays an important role in recovery. In some cases due to the smaller cathode surface, increasing the initial metal concentration will decrease the recovery rate. This is because all active sites of the cathode become occupied with the earliest deposition. Therefore it is essential to optimize conditions in order to find the best correlation between initial metal concentration and available cathode surface area.

3.1.3. Effect of supporting electrolyte concentration

The effects of supporting electrolyte concentration were studied because of its role in controlling the conductivity of solutions. The influence of using different concentrations of NaCl (0.1 and 0.2 M) as supporting electrolyte on the recovery of gold is presented in Fig. 2(d). It is shown that a higher concentration of NaCl in the catholyte compared to that in the anolyte increases the recovery rate. This could be due to the increase in stability of the gold chloride complexes [28] and enhanced solution conductivity [29]. In addition, more concentrated chloride ions in the catholyte compartment would positively enhance the movement of Cl^- ions from catholyte to anolyte through the anion exchange membrane. Since the cathode is very close to the ion-exchange membrane, this event will lead to an increase convection process at the cathode\catholyte interface. The other positive effect of increasing NaCl supporting electrolyte concentrations in the catholyte solution could be explained in terms of increasing $Na^+ AuCl_4^-$ formation, which in turn, has a faster diffusion rate compared to the $AuCl_4^-$ complex. The faster movement of sodium ions drags the oppositely charged $AuCl_4^-$ ions along. In other words approaching the negatively charged cathode surface becomes easier for the negatively charged $AuCl_4^-$.

3.1.4. Effect of membrane

To assess the permeability of the various membranes used in this study, the concentration of gold in the anolyte solution was determined by AAS. For all cases where a cation exchange membrane was used, there were considerable amounts of gold ions (around 30 to 50% of the initial Au(III) concentration) in the anolyte which shows that Au(III) had been transferred through the membrane. When an anion exchange membrane was used, the concentration of Au(III) in the anolyte was negligible. Better gold recoveries were obtained when the Neosepta anion exchange membrane was used compared to that with the Mega Ralex membrane.

Table 3. Membrane information

Membrane type	Thickness [mm]	Resistance area R_A [$\Omega.cm^2$]
Cation Mega, CM(H) PAD	< 0.65	< 8.5
Anion Mega, AM(H) PAD	< 0.70	< 7
Anion Neosepta, AMX	0.14	2.4
Cation Neosepta, CMX	0.17	3

This outcome could be caused by the thickness and resistance of the membrane because the Neosepta anion exchange membrane is thinner and less resistant than the Mega membrane. The information about both types of membranes is presented in Table 3. The anion exchange membrane from Neosepta was used in all experiments.

3.2. Polarization studies

In order to investigate the performance of a system with different cathode materials, cathode polarization curves were obtained. In this case, the potential of the cathodes was plotted vs. its current density which was calculated based on the geometric cathode area that was in contact with the catholyte. Fig. 3(a) shows that the RVC electrode performs better as a cathode compared to other cathode materials.
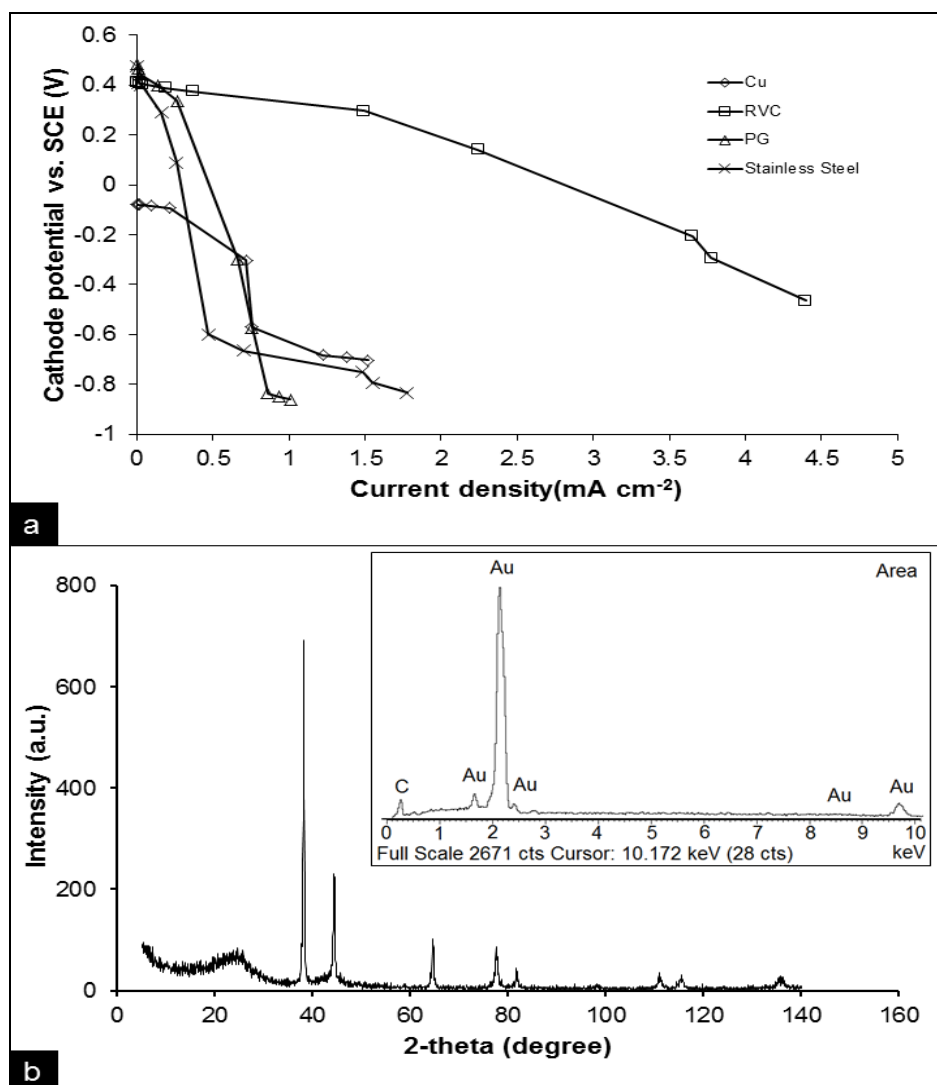

Figure 3. (a) Cathodic polarization curves for systems utilizing RVC, PG, Copper and stainless steel plates as cathodes with 250 mg L^{-1} Au(III) in 0.2 M NaCl and 0.4 M NaH$_2$PO$_4$ at pH 7. (b) X-ray diffraction pattern of metallic gold. The inset depicts the EDX of the cathode substrate after the gold deposition process.

A maximum current density of 3.78±0.066 mA/cm^2 was obtained with RVC which is higher compared to that obtained using other cathode materials. The overall polarization of the system with RVC is significantly smaller compared to other substrates. At a current density of 1.49±0.004 mA/cm^2,

a decrease of 0.130 V is observed for the RVC compared to a decrease of more than 1.349 V with PG over the same value of current density. The other cathode materials also exhibited high cathode polarization similar to the PG electrode.

The open circuit voltages (OCV) for different cathodes are listed in Table 2. As shown in Fig. 3(a), it can be concluded that the RVC cathode will perform better compared to other cathode materials. The greater polarization of PG, stainless steel and copper electrodes indicates slower kinetics. The following section will describe how the PG electrode behaved similarly to the two dimensional stainless steel and copper electrodes in the recovery of gold from chloride media. The smaller cathode polarization and higher achieved current density indicate that the RVC is best cathode choice compared to the other cathode materials. However, by using the copper and stainless steel cathode, deposited gold would be collected more easily at the end of the experiment rather than a carbon based electrode. The current efficiency and rate of recovery in these cases tend to be very low compared to the RVC.

3.3. Morphology of gold deposits

3.3.1. XRD and EDX Studies

To confirm the formation of metallic gold, XRD and SEM-EDX analyses were carried out on gold deposited from 250 mg L^{-1} Au(III) solution on RVC for 90 min. The XRD pattern in Fig. 3(b) shows that the 2θ values of the peaks at 38.2, 44.4, 64.6, 77.5 and 81.7^o match those of metallic gold peaks which verified the formation of elemental gold during the deposition process [30]. The EDX in the inset of Fig. 3(b) also shows deposition of metallic gold.

3.3.2. SEM analysis

Gold deposition from 500 mg L^{-1} Au(III) solution was carried out for 30 s, 60 s and 2 h on both the RVC and PG cathodes. Then the cathodes were analyzed using SEM as shown by the micrographs in Figs 4(a) – (f).

The average size range of gold deposits on PG and RVC after 30 s and 60 s is between 60- 300 nm. It was observed that over time, gold aggregates were formed. The deposited gold was granular and flower shaped when PG was used. The deposited particles were spherical, granular and more homogeneous and smaller in size when RVC was used. The particles tended to form sponge-like deposits, by increasing recovery time. As observed, the gold produced dendrites when copper and stainless steel were used as cathodes. A dendrite is a crystal with a tree-like branching structure and this kind of micro-structure which is formed during deposition plays an enormous role in the properties of the solid material. In fact, almost all freshly crystallized gold particles are composed of many dendrite crystals stuck together. Investigations on the effects of different pH values and recovery time in order to achieve gold nanoparticles which could be applied as electrocatalysts are currently underway.
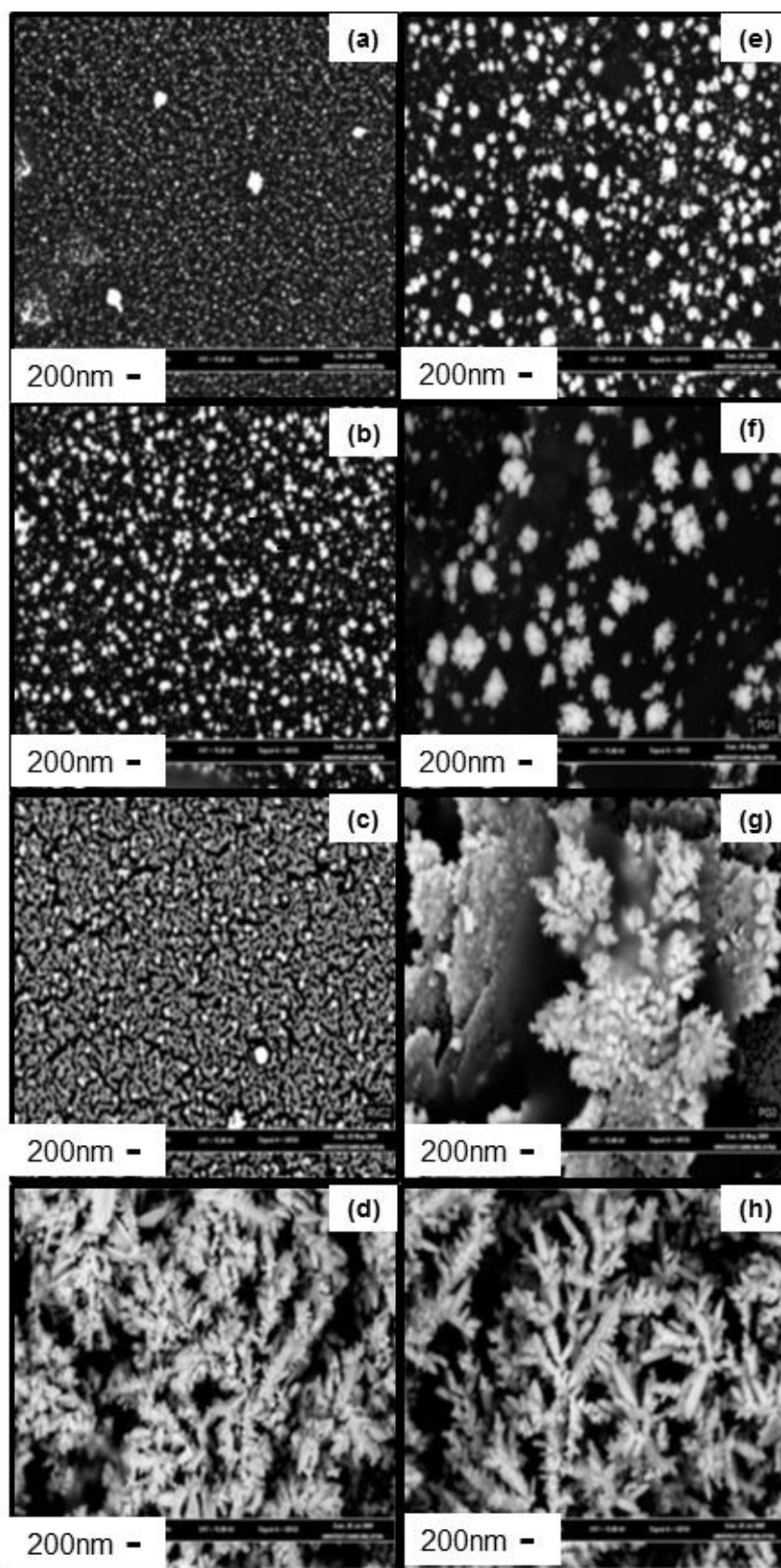
Figure 4. SEM images of gold electrodeposition at different times and on different substrates: (a) RVC-30s, (b) RVC-60s, (c) RVC-2 h, (d) copper sheet -2 h, (e) PG-30s, (f) PG-60s, (g) PG-2 h, (h) stainless steel-2 h.

4. CONCLUSIONS

In this work, studies on the electrogenerative deposition of gold onto various cathode materials from chloride solutions were carried out. RVC enhanced the rate of gold recovery when compared to other electrodes used in this study with more than 90% of gold recovered at pH 7.0 within 1 h of operation. The electrogenerative process provides an alternative for gold recovery with a clean and environmental friendly process to recover this precious metal.

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