

Electrochemical Redox of Hg^{2+} Mediated by Activated Carbon Modified Glassy Carbon Electrode

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Received: 9 April 2010 / Accepted: 15 May 2010 / Published: 30 May 2010

The use of a glassy carbon electrode (GCE) modified by activated carbon (AC) mediates the redox of mercuric chloride (HgCl_2) in 0.1 M aqueous solution of potassium chloride (KCl) supporting electrolyte. During cyclic voltammetry, an oxidation and two reduction peaks of Hg^{2+} were appearing at +200, +680 and +100mV respectively, versus Ag/AgCl. The redox current of Hg^{2+} was enhanced by two folds at AC modified GCE and about five folds in acidic media. The oxidation peak of Hg^{2+} was shifted to lower potential by approximately 5mV and for the reduction peak was shifted to 0 mV in acidic solution at AC/GCE. The sensitivity under condition of cyclic voltammetry was significantly dependent on pH, concentration of AA and temperature. Interference with Hg^{2+} was observed in different metal ions, such as Ca^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} and Cd^{2+} . The current enhancement appeared and causes further increase in the reduction peaks of Hg^{2+} , in contrast the oxidation current decrease when increase the concentration of the interference metals. Excellent analytical recovery results were observed with using blood sample and seawater. The surface charge determined by chronocoulometry (CC) of Hg^{2+} at AC/GCE in acid solution was more conductive than use of GCE. Diffusion coefficient determined by chronoamperometry (CA) for Hg^{2+} at AC/GCE in presence of AA was promising results.

Keywords: Activated carbon. electrocatalysis. AC/GC electrode. HgCl_2 . cyclic Voltammetry

1. INTRODUCTION

Activated carbons (ACs), which are produced by either thermal activation or chemical activation, have a large surface area, a broad range of pore size distribution and extremely cheap. Activated carbons consist of small hexagonal carbon rings, which are called “graphene sheets”. Different size orientation and stacking of these sheets can be achieved by adjusting the carbon preparation method. But, in general, an activated carbon has an amorphous structure and lacks long-range three-dimensional order [1, 2].

Cyclic voltammetric studies of the influence of surface chemistry on the electrochemical behavior of powdered AC electrodes PACE in the presence of selected heavy metal ions Pb^{2+} , Hg^{2+} , Cd^{2+} in bulk solution and pre-adsorbed on carbon were carried out. Under certain circumstances, the greater current signal obtained by modified carbon electrode has been attributed to the presence of "edge effect" of microparticles of activated carbon. The adsorption capacities of the modified AC samples towards the heavy metal ions were estimated. The mechanisms of adsorption processes of metal species on AC surfaces were extensively studied and described on the basis of their electrochemical behavior [3,4].

The reduction of Hg^{2+} at a GCE in nitrate, perchlorate and sulphate solutions at various pH values has been studied by rotating ring-disk voltammetry and linear sweep voltammetry. The reduction proceeds directly to metallic mercury in a single step, with the take-up of two electrons. Linear sweep voltammetry at a stationary electrode indicates that the reduction of Hg^{2+} behaves reversibly at low sweep rates but irreversibly as the scan speed increases [5].

Hg^{2+} , Pb^{2+} , Ag^+ and Cu^{2+} cations have been adsorbed onto a new thick-walled form of mesoporous silica having a minor amount of microporosity and then voltammetrically reduced after the fabrication of a carbon paste-mesoporous silica composite electrode which has been placed in an aqueous acidic electrolyte medium. The following well-defined voltammetric responses are observed for the systems studied: $\text{Hg}^{2+} \rightleftharpoons \text{e}^- \text{-Hg}^+ \rightleftharpoons \text{e}^- \text{-Hg}$. Notable features relative to voltammograms obtained when the metal ions are reduced directly in the solution phase are the stabilization of the Hg^+ oxidation state, the linear dependence of peak heights on acid concentration in the molar concentration region and the absence of metal stripping characteristics when metal is reoxidised [6].

Mercury reduction and oxidation on ultrathin gold electrodes (Vasjari et. al. 2007) were investigated. The former by simultaneous voltammetry and surface plasmon resonance (SPR). The angle dependencies of SPR signal were analyzed quantitatively. The results indicate partially reversible formation of amalgam with optical properties in between of optical properties of mercury and gold. Up to 12% content of mercury in the gold layer is suggested [7].

Inverse voltammetric signals during Hg^{2+} oxidation-reduction in the presence of potentiated water, lithium chloride, and mercury nitrate were studied by alternating-current inversion voltammetry. Potentiated substances modified oxidation-reduction processes in the electrochemical system. Potentiated solutions of Hg^{2+} increased the effective concentration (activity) of mercury ions. The effect was most significant in the presence of mercury nitrate in homeopathic dilutions $\text{C}_6+\text{C}_{12}+\text{C}_{24}$. The results indicate that potentiated substances specifically modulate kinetic and thermodynamic characteristics of solutions containing the same compounds [8].

AC modified with a liquid anion exchanger (Amberlite LA2) was used for the voltammetric determination of Hg^{2+} . Mercury is preconcentrated, as tetrachloromercurateII, on to the surface of the modified electrode only by the ion-exchange effect of the modifier without application of potential. After exchange of the medium the accumulated amount of Hg^{2+} is determined by differential pulse anodic stripping voltammetry in a blank electrolyte solution [9].

In this work, AC modified mediators are fixed on the GC electrode surface by mechanical attachment method to fabricate AC/GCE. Redox peaks of Hg^{2+} have good electrochemical behavior in terms of stability and high sensitivity.

2. EXPERIMENTAL PART

2.1. Chemicals and materials

Activated carbon from Fluka at a purity of 98% was used. Other chemicals and organic solvents used were of analar grade and used as received from the manufacturers (KCl , HgCl_2 , MnCl_2 , LiOH , HCl , NaOH , NH_4Cl , CdCl_2 , CuCl_2 and MgCl_2). Distilled water was used for the preparation of aqueous solutions. All solutions had the dissolved oxygen removed with pure nitrogen gas for fifteen minutes prior to making the voltammetric measurements.

2.2. Instrumentations and apparatuses.

Electrochemical workstations of Bioanalytical system (Inc. USA: Models BAS CV 50W) with potentiostat driven by electroanalytical measuring softwares were connected to PC computer to perform cyclic voltammetry CV, CC and CA. An Ag/AgCl (3M NaCl) and platinum wire were used as a reference and a counter electrode, respectively. The working electrode used in this study was 3mm diameter unmodified GC electrode and AC modified GCE using by mechanical method.

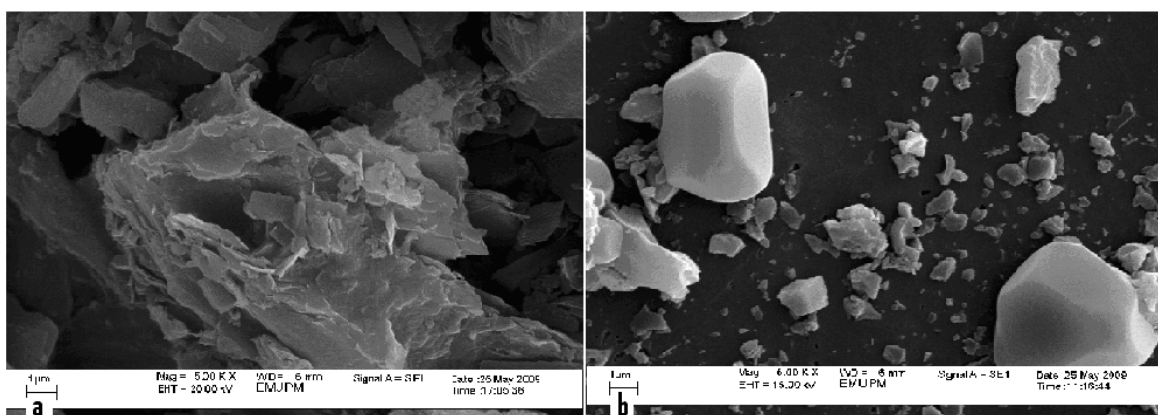


Figure 1. Scanning electron micrographs of AC microparticles mechanically attached to a basal plane pyrolytic graphite electrode (a) before and (b) after electroanalysis with Hg^{2+} .

2.3. Preparing for AC modified GC electrode and SEM.

A mechanical attachment technique [10,11] used direct use of AC in powder form and modified GCE by abrasively adhere AC microparticles onto the GC electrode surface. Scanning Electron Microscopy (SEM) was performed to look at the AC microcrystals on a graphite electrode surface. SEM image of AC attached on 5 mm diameter basal plane graphite electrode exhibits an array of microcrystals with sizes ranging from 0.2 μm diameter with the magnification of 5000 times Figure 1a.

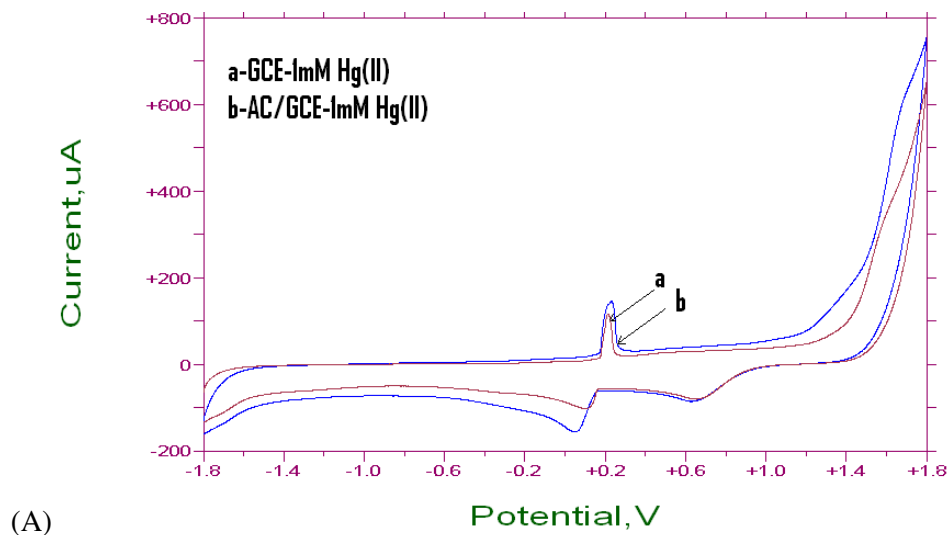
Figure 1b illustrated slightly larger in size than those obtained before electrolysis, with size of ca. 3 μm in diameter indicating the presence of a surface process of solid-solid transformation and attributing to the presence of Hg^0 , the reduced species of Hg^+ and Hg^{+2} .

3. RESULTS AND DISCUSSION

3.1. Enhancement studies

3.1.1. Effect of different electrodes

Figure 2a and 2b show the oxidation and reduction current peaks of Hg^{2+} was considerably enhanced by 2 times with the second reduction peak shifting of about 200 mV towards origin 0mV when AC/GCE was used in comparison with GCE. Evidently degree of sensitivity response increases by modified AC/GCE. The reduction peaks of Hg^{2+} appears more discernable when AC/GC electrode is used as compared with bare GC electrode. Reduction peaks become even more pronounced and enhanced by two times at the electrode surface of AC/GCE. The observation of one oxidation and two reduction peaks appears to be dependent on pH, and temperature conditions.



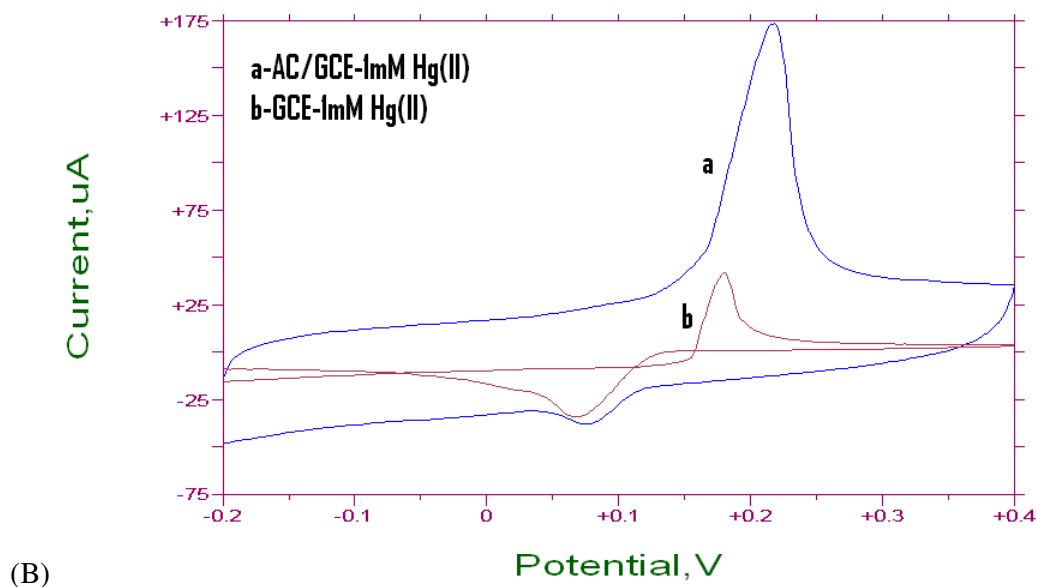


Figure 2. (A) cyclic voltammogram of 1mM Hg^{2+} in 0.1M KCl as supporting electrolyte at 100 mV s^{-1} using (a) AC/GCE (b) GCE, and (B) voltammogram of oxidation-reduction peaks for 1mM Hg^{2+} in 0.1M KCl, pH 3 at 100 mV s^{-1} using (a) AC/GCE (b) GCE versus Ag/AgC

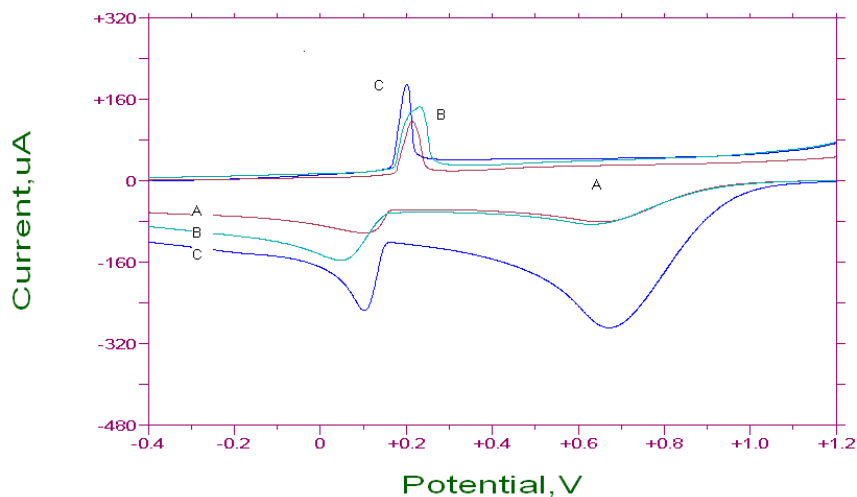


Figure 3. Voltammograms for effect of AA in the redox peaks of 1mM Hg^{2+} (A) bare GCE, without AA (B) AC/GCE without AA and (C) AC/GCE with 1mM AA in 0.1M KCl, 100 mV s^{-1} versus Ag/AgCl.

3.1.2. Effect of Ascorbic Acid

Figure 3 shows the effect for the oxidation and reduction current peaks of Hg^{2+} with and without AA on modified AC/GC electrode using cyclic voltammetry. It was observed that the oxidation peak of Hg^{2+} appeared at +200mV and two others reduction peaks at +650 and +100mV. It

was considerably enhanced by 3-4 times in presence of 1mM AA on AC/GCE. Moreover, the second reduction peak of Hg^{2+} appears at +100mV indicate the reduction of mercury ion to mercury metal as a white color precipitated on the modified electrode as in equation 1.



3.2. Optimization of conductive effect

3.2.1. Effect of varying Temperature

Effect of temperature on the reduction process of Hg^{2+} was studied. The current increases gradually at the temperature of 5 to 80°C. Figure 4 is plot of \log (reduction current) of Hg^{2+} versus reciprocal of temperature which is found to be fairly linear in agreement with thermodynamic expectation of Arrhenius equations 2 and 3 [12].

$$\sigma = \sigma^0 \text{Exp} (-E_a/RT) \quad (2)$$

$$D = D^0 \text{Exp} (-E_a/RT) \quad (3)$$

Where: σ / D are conductivity / diffusibility and σ^0 / D^0 are standard conductivity / the initial diffusibility.

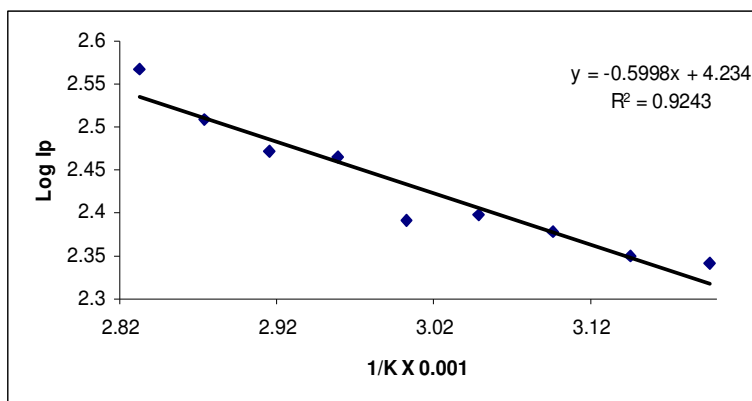


Figure 4. Dependence of oxidation current of Hg^{2+} as a function of temperature on AC/GCE.

From slope of linear relationship the value of activated energy of Hg (II) is $E_a = 11.5$ KJ/mol compared with another works were around $E_a = 16.30-26.75$ KJ/mol [13, 14]. The conductivity of AC/GCE with increasing temperature also plays a significant influence on the activation energy for diffusion of the substrate of interest, E_a . Figure 5 shows that an increase in temperature from 10 to

80°C is accompanied of a sharp increase in current causes shifting of oxidation potential towards higher value and decrease in current of reduction peaks and causes shifting to higher potential. Evidently, simultaneous application of the use of AC/GCE and increase in temperature exert a greater electrocatalyst effect. However, while use at high temperature can give an increase in temperature, in practical sense application need to be continued close to room temperature, 25°C [15].

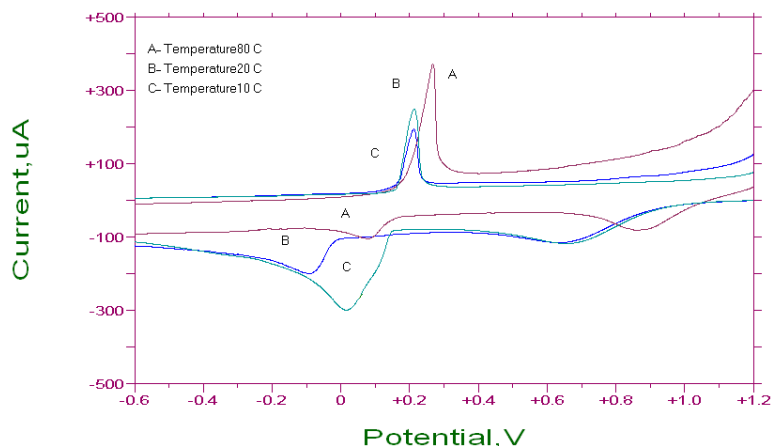
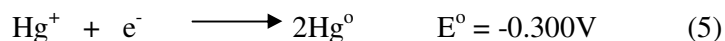
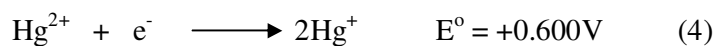


Figure 5. Voltammogram for the oxidation and reduction of 1mM Hg^{2+} in 0.1M KCl at AC-GCE at different temperatures (A) 80°C (B) 20°C and (C) 10°C, 100mVs⁻¹ vs. Ag/AgCl.

8.3.3.2. Effect of varying pH

The solution pH was varied from 2 to 12 to determine its effect on the catalytic oxidation-reduction of Hg^{2+} at the AC modified GC electrode. (a) Acidic solution at pH 2 to 6. It was observed that the oxidation current of Hg^{2+} gradually increases linearly with lowering of pH from 6 to 2 accompanied by linear shift in oxidation potential as described by the equations, $I(\text{uA}) = -23.126 \text{ pH} + 287.67$ with correlation coefficient of $R^2 = 0.9941$ and $E(\text{mV}) = -5.546 \text{ pH} + 224.09$ with $R^2 = 0.9267$; the two reduction peaks of Hg^{2+} at +500 and -300mV were shifted to higher potential at +600 and 0mV respectively, with both the current peaks increased by about three times, while the reoxidation peak increased in about two folds and shifting towards origin potential as shows in Figure 6, the mechanism of these reduction process is explained as in the following equations (4 and 5):



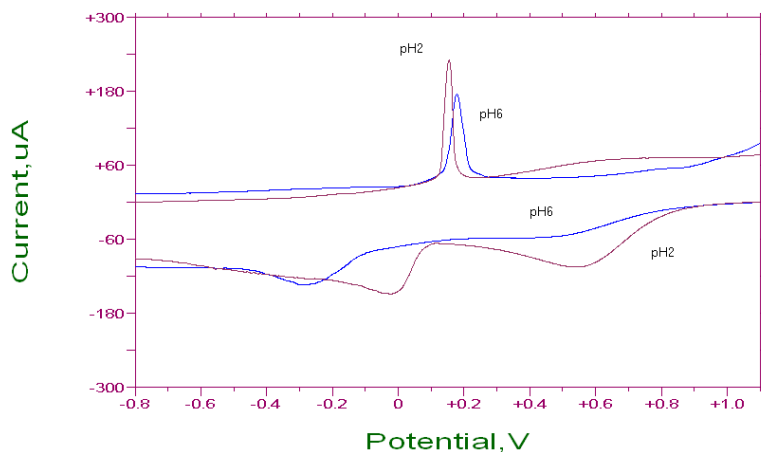


Figure 6. Voltammograms for effect different pH ranging from 2-6 for the redox process of 1mM Hg^{2+} in 0.1M KCl vs. Ag/AgCl at AC-GCE, 100mVs^{-1} .

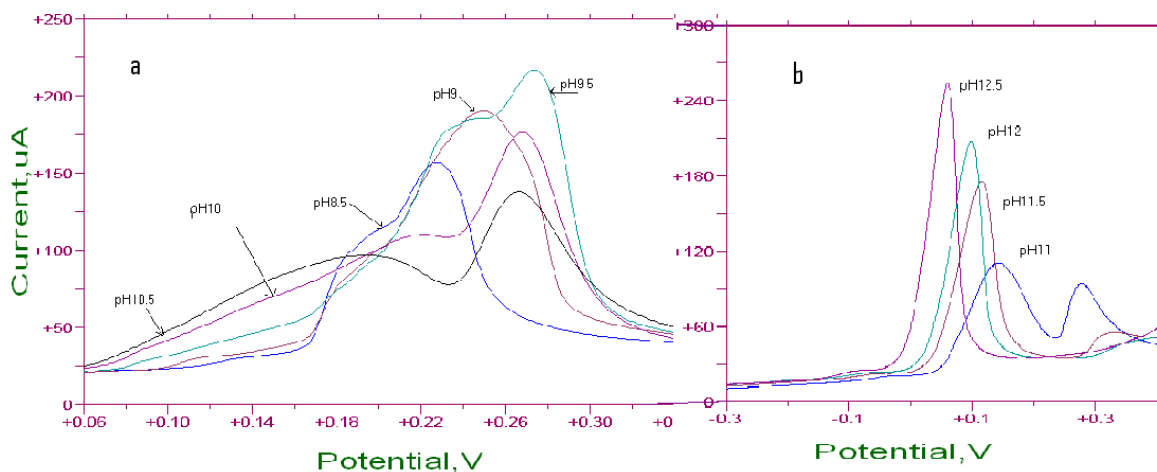


Figure 7. The effect pH (a) pH 8.5 – 10.5 (b) pH 11 – 12.5 on the oxidation current peaks of 1mM Hg^{2+} in 0.1M KCl vs. Ag/AgCl at AC/GCE, 100mVs^{-1} .

(b) Alkaline solution at pH from 8.5 to 12.5, a new phenomena was noted in the oxidation process associated with $\text{Hg(II)/Hg(I)/Hg(0)}$ couples in different alkaline solutions. At pH 8.5 to 10.5 the two oxidation peaks instead of the usual one were observed, one with high current and at high potential between +230 to +280mV while the one with lower current situated between +190 to 220mV. In contrast, the properties of split oxidation peak is different at pH 11 to 12.5 as the current peaks changes in magnitude and merge to form one oxidation peak at pH 12.5, with peak potential shifted towards the origin (Figure 7a and 7b). The phenomena can be attributed to the occurrence of two processes during the oxidation of Hg^+ and Hg^0 in alkaline solution as in the following equations 6 and 7 [16].

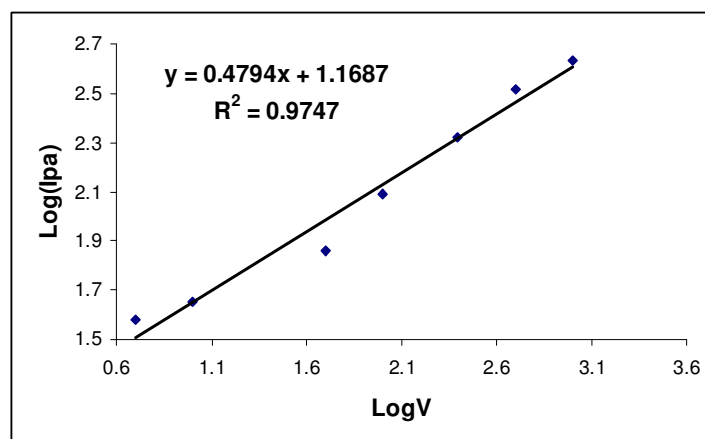
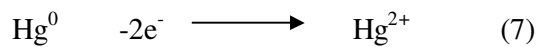
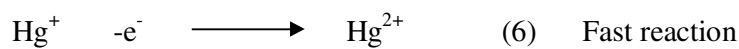


Figure 8. Plot of Log (Ipa) reductive current versus LogV scan rate of 1mM HgCl₂ in 0.1M KCl using AC/GCE versus Ag/AgCl.

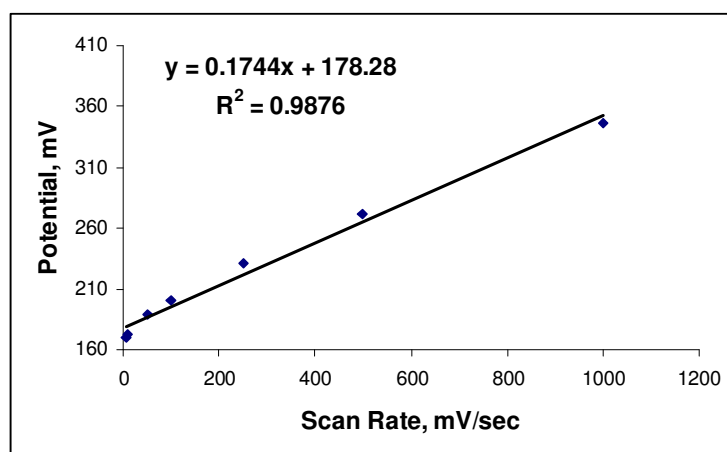


Figure 9. Plot of Potential versus scan rate of 1mM HgCl₂ in 0.1M KCl using AC/GCE versus Ag/AgCl.

3.3.3. Effect of varying scan rate

A reasonably linear dependence of Hg²⁺ oxidative current on scan rate is described by $y = 0.4794x - 1.1687$, $R^2 = 0.9747$. The slope of log I_p (oxidative current) versus log V (scan rate) is 0.48 which is agreed well with the theoretical slope of 0.5 for diffusion controlled process as in Figure 8 indicating the redox currents obtained is predominantly under diffusion controlled.

Figure 9 shows the relationship between oxidative potential and scan rate of Hg²⁺, oxidation peak at 170mV in low scan rate (5mV/sec) is shifted linearly to 307mV at a high scan rate

(1000mV/sec). The linearity can be described by $Y=0.1744X+178.28$ ($R^2=0.9876$). By extrapolation the linear line towards the origin, the intercept obtained at zero current produces a zero current potential ($E^{0,1}$) of 170mV for the oxidation of Hg(II) ion at AC/GCE.

8.3.4 Calibration Graph

The calibration plot (Fig. 10) was performed at the AC/GCE in 0.1 mM – 0.6 mM Hg^{2+} solutions with a good linearity of anodic current versus Hg^{2+} described by $Y= 90.857X+194.53$, $R^2=0.9792$, and excellent sensitivity response of 90.86 mA/mM.

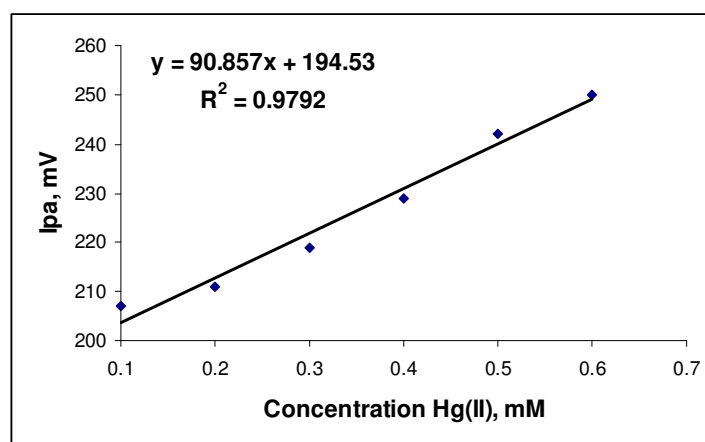


Figure 10. Plot of reduction current versus different concentration 0.1-1mM $HgCl_2$ in 0.1M KCl using AC/GCE versus Ag/AgCl.

3.5. Interference study

3. 5.1. Effect of heavy metals

Possible interference of some metals in the voltammetric determination of 1mM Hg^{2+} was studied by addition of the interfering ion to a solution containing 1mM of Mn^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} and Ca^{2+} using the optimized conditions at pH6. The results in table 1 show positive interference of all ions on the oxidation-reduction peaks of Hg^{2+} by increasing the oxidation-reduction current by 2 to 3 folds and shifting to lower potential except in Ni^{2+} which decreasing the both current oxidation-reduction peaks shifting to higher potential.

Table 1. Effect of different heavy metals (1mM) on oxidation and reduction peaks of 1mM Hg²⁺ using AC/GCE.

Heavy Metals	I _{pa} , uA	E _{pa} , uA	I _{pc(I)} , uA	E _{pc(I)} , mV	I _{pc(II)} , uA	E _{pc(II)} , mV
Hg ²⁺ only	150	+200	80	+700	155	+50
Hg ²⁺ +Mn ²⁺	177	+156	627	+746	263	+41
Hg ²⁺ +Cd ²⁺	257	+216	298	+647	347	+57
Hg ²⁺ +Cu ²⁺	192	+167	347	+636	218	+35
Hg ²⁺ +Cd ²⁺	252	+193	317	+669	332	+57
Hg ²⁺ +Ni ²⁺	97	+210	74	+587	120	+134

The interfering effects of Mn²⁺, Cd²⁺, Cu²⁺, Cd²⁺ and Ni²⁺ on the reduction of Hg²⁺ in 1:1 ratio were investigated using the modified electrode AC/GC during CV. In general, all metal ions except Ni²⁺ under studied pose positive interference as the redox current of Hg(II)/Hg(I)/Hg(0) couples increases further in the presence of these interfering metal ions (Table 1).

3.6. Application study

3.6.1. Recovery rate of Hg²⁺ in blood

Calibration of Hg²⁺ in mouse blood was carried out by using blood sample as supporting electrolyte and a known amount of Hg²⁺ was spiked into the blood (Figure 11).

The redox of Hg²⁺ in blood sample as a supporting electrolyte gives a calibration plot of good linearity, $Y=19.296X + 34.536$ and the correlation coefficient $R^2=0.9949$ with high sensitivity response of $19.20 \mu\text{AmM}^{-1}$ and good detection limit of Hg²⁺ in blood.

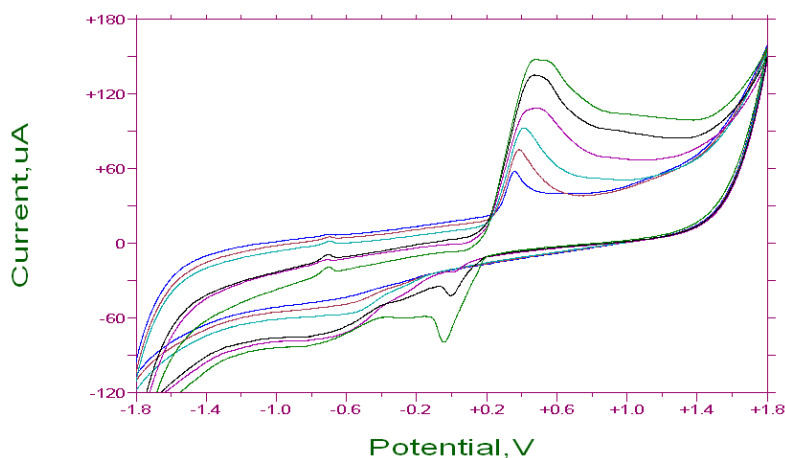


Figure 11. Cyclic voltammograms for the effect of blood sample on redox process of different concentration of 0.5-6 mM Hg²⁺ versus Ag/AgCl on AC/GCE; 100 mVs⁻¹.

The recovery of $102.75 \pm 1.9\%$ was obtained after the addition of 0.9 mM Hg^{2+} in to blood sample as in table 2 while recovery of $95.78 \pm 4.9\%$ was obtained after the addition of 4.5 mM Hg^{2+} in to blood sample as in table 3.

Table 2. Recovery rate of 0.9 mM Hg^{2+} added in to blood samples at AC modified GCE.

Number of sample Standard	Concentration	Recovery	Mean	Relative
	of Hg^{2+} (mM)	Rate (%)	Recovery %	Deviation %
1	0.97	97.0		
2	0.85	85		
3	0.95	106		
4	1.00	111	102.75	1.9

Table 3. Recovery rates of 4.5 mM Hg^{2+} added in to blood samples at AC modified GCE.

Number of sample Standard	concentration of Hg^{2+}	Recovery	Mean	Relative
	(mM)	Rate (%)	Recovery %	Deviation %
1	4.5	100		
2	4.0	88.9		
3	4.25	94		
4	4.6	101		
5	4.3	95	95.78	4.9

3.6.2. Recovery rate of Hg^{2+} in seawater

Recovery experiments of Hg^{2+} in seawater were evaluated using direct calibration of $Y=37.071X + 214.71$, $R^2=0.9876$. The recovery of $95.2 \pm 4.15\%$ was obtained after the addition of 0.5 mM Hg^{2+} in to seawater sample as in table 4.

Table 4. Recovery rate of 0.5mM Hg²⁺ added in to seawater sample at AC modified GCE

Number of sample Standard	concentration of Hg ²⁺ (mM)	Recovery Rate (%)	Mean Recovery %	Relative Deviation
1	0.5	100		
2	0.48	96		
3	0.49	98		
4	0.46	92		
5	0.45	90	95.2	4.15

3.7. Chronoamperomogram (CA) and Chronocoulomogram (CC) studing

Figure 12 shows the monotonous rising and decaying current transient in accordance to the theoretical expectation of the Cottrell equation [17, 18]. Based on the diffusion process to a planar electrode. Diffusion coefficient (D) of $1.756 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ was determined for Hg²⁺ ion in 0.1 M KCl using AC/GC as a working electrode. It was found that the AC/GCE has a total charge transferred of $46.3 \mu\text{C m}^{-2}$ in AC in the presence of ascorbic acid (AA), while the low charge transferred of $4.0 \mu\text{C m}^{-2}$ in Hg²⁺ with out AA. This shows that AC/GCE with attendance of AA is more reducible than its absence as in Figure 13.

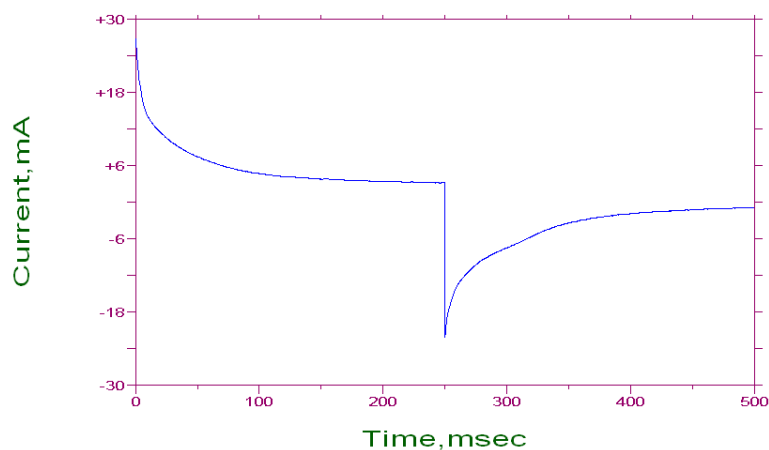


Figure 12. CA or Cottrell plot obtained for the redox of 1 mM Hg²⁺ in 1 mM AA in 0.1 M KCl electrolyte at AC/GCE. Potential was scanned in a negative direction from -1800 to +1800 mV with 250 msec. pulse width.

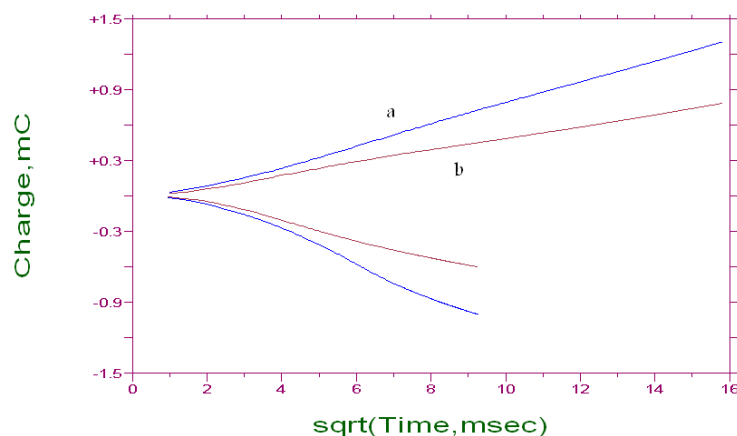


Figure 13. CC or Anson plot of charge versus $t^{1/2}$ for redox of 1 mM Hg^{2+} in (a) 1 mM AA at AC/GCE and (b) without AA at bare GCE in 0.1 M KCl vs. Ag/AgCl.

4. CONCLUSIONS

AC modified GCE has been successfully fabricated by mechanical attachment method, which is shown to be able to mediate effectively in redox of Hg^{2+} with significant current enhancement. The observed current enhancement can be attributed to the presence of a larger surface area and associated “edge effect” of an array of AC microparticles. The redox peaks of Hg^{2+} was dependent on the concentration AA, pH and temperature. The interference studies with heavy metals Mn^{2+} , Ni^{2+} , Cu^{2+} , Ca^{2+} and Cd^{2+} were promising with the redox current peaks of Hg^{2+} . Excellent recovery rates were obtained from the analysis of Hg^{2+} in seawater and mouse blood sample. The magnitude of the surface charge determined by Anson's plot shows that AC/GCE was more conductive (large current transferred) compared with GCE. Diffusion coefficient D has been determined for the redox of Hg^{2+} under the voltammetric conditions mentioned above.

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