Determination and stripping of lead ions at disorganised self-assembled monolayer modified gold piezoelectrode

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ABSTRACT

Deposition and stripping of lead ions at thiol based disorganised monolayer modified gold piezoelectrodes was studied by cyclic voltammetry (CV) and electrochemical quartz crystal nanobalance (EQCN). Gold electrodes modified with 3-mercaptopropionic acid and 1,3-dimercapto propane sulphonic acid were studied. Due to the proximity of the potentials for the Pb deposition and thiol reductive desorption, successful achievement of a deposition and stripping voltammetry methodology for determination of low concentrations of Pb^{2+} was achieved. However by comparison of the CV and EQCN data and consideration of the mass changes per mole electrons transferred in light of the other species present in solution, possible mechanisms are put forward for the desorption and stripping of Pb^{2+} at thiol modified gold electrodes.

Key words: Lead, electrochemical quartz crystal nanobalance, thio, cyclic voltammetry, self-assembled monolayer, desorption.

INTRODUCTION

Previously, the viability of disorganised monolayer coatings on gold electrodes surfaces as means for protection of that surface from adsorption and fouling by sample constituents other than the analyte species was demonstrated[1-4]. Disorganised monolayer coatings were created by use of thiol compounds having short hydrocarbon chains and bulky and charged end chain substitutions[5-8], thereby possessing the three molecular components necessary for the disorganised monolayer formation: the thiol bonds spontaneously to the gold surface, the short hydrocarbon chain minimised lateral Van der Walls interactions which, in combination with the bulky charged end chain groups, disallowed formation of a self-assembled, ordered monolayer. The gold electrode surface was protected from the adsorption of both synthetic and natural surfactants[9-10] but most importantly also allowed permeation of copper ions to the electrode surface. These ions were electrolytically deposited as the copper and voltammetric stripping of the copper produced an analytical signal. This methodology is referred to as underpotential deposition and stripping voltammetry for convenience. Mercaptoacetic acid (MAA) and mercapto sulfonic acid (MES) coated electrode were used for the quantitative determination of copper in real samples matrices with no sample preparation necessary other than dilution or addition of electrolyte.

Attempts to extend the range of metals that can be detected using an electrode modified with a thiol disorganised monolayer are presented here. Due to its high toxicity, Pb^{2+} was selected as another target analyte. Pb deposition at both Au and Ag electrodes was intensively investigated by Kirowa and colleagues[11-12], who demonstrated the

possibility of using deposition-SV for determination of Pb^{2+} concentration. Moreover, at a gold electrode modified with mercaptopropnae sulfonic acid (MPS). Arrigan et al. reported an apparently enhanced voltammetric signal. However, during the deposition of the Pb monolayer, desorption of the thiol monolayer was also observed. The proximity of Pb desorption potential and of the thiol desorption constitutes an interesting electroanalytical challenge.

It was reported that the presence of chloride anions enhanced the Pb deposition stripping signal on both Au and Ag electrodes[13]. The presence of nitric acid gave the highest analytical response compared with sulfuric, perchloric and hydrochloric acids.

Cyclic voltammetry (CV) and electrochemical quartz crystal microgravimetry were used to study the deposition of Pb^{2+} at 3-mercaptopropionic acid (MPA) and 1,3-dimercapto propane sulphonic acid (DMPS) modified gold electrodes. The aim of the work was to ascertain whether Pb^{2+} was a possible valid analytical target for the stripping at disorganised monolayer modified gold electrodes.

EXPERIMENTAL

Electrochemical experiments were carried out with a PGSTAT20 potentiostat (Ecochemie, Holland). All experiments were performed within a Faraday cage. The working electrodes were gold electrodes coated quartz crystals for geometric area was $0.23 \ cm^2$. The quartz crystals had a fundamental frequency of 10MHz. The density, ρ_q and the shear modulus a of quartz were 2.684 g cm^{-3} and 2.947×10^{10} g cm^{-1} s^{-2} , respectively. Using Sauerbrey, (Eq.1), α 1 Hz change in frequency corresponded to a 1.1 ng change in mass on the electrode surface.

$$\Delta f = -\left(\frac{2f_0^2}{\rho_q V_q} \right) \frac{\Delta M_q}{A} \qquad ...(1)$$

Due to the fragility of the gold coated quartz crystal (they did not withstand the

potentiodynamic cycling in sulfuric acid electrochemical pre-treatment usually used with poly crystalline gold disc electrodes[14]; this was attributed to the presence of the chromium adhesion layer between the gold and quartz, they were cleaned by rinsing them with dilute nitric acid solution and de-ionised water. The reference electrode was a saturated calomel electrode SCE, (CH Instruments) and the counter electrode was a platinum gauze (CH Instruments).

The electrode modification procedure was that described previously[13]. The electrode was immersed for 5 minutes at open-circuit in aqueous solution containing 5mM of the modification reagent selected (MBA) or (DMPS) and 0.1 M perchloric acid. The electrochemical cell and other glassware were cleaned with concentrated nitric acid (69%) before use. They were then rinsed with abundant de0ionised water. The thiol reagents selected (MBA) or (DMPS) for the modification of the gold electrode (working electrode) were of the highest purity commercially available. They were used without further purification to prepare the modification solution. Modification solutions were prepared before experiments on a daily basis. All reagents used for this study were purchased from Sigma-Aldrich England, Ltd.

RESULTS AND DISCUSSION

General observations

Initially, Pb potential deposation at a bare gold electrode was investigated by CV and EQCM in the potential range between 0.2 and -0.8 V (Fig.1). A weak cathodic current was measured between -0.1 and -0.2V which did not have any corresponding frequency change on the EQCM data.

The cathodic peak at -0.40V corresponded to potential deposation of Pb; this was accompanied by an increase in the mass at the electrode surface. The bulk deposition of lead occurred at -0.60V. On the reverse scan (-0.8 V back to 0.3V) it can be noted that the frequency continued decreasing until the stripping of the bulk deposit occurre at -0.5V (the anodic peak). During this process a marked increase of the frequency change confirmed that Pb atoms were stripped from the surface and dissolved into the solution. A mass loss (frequency
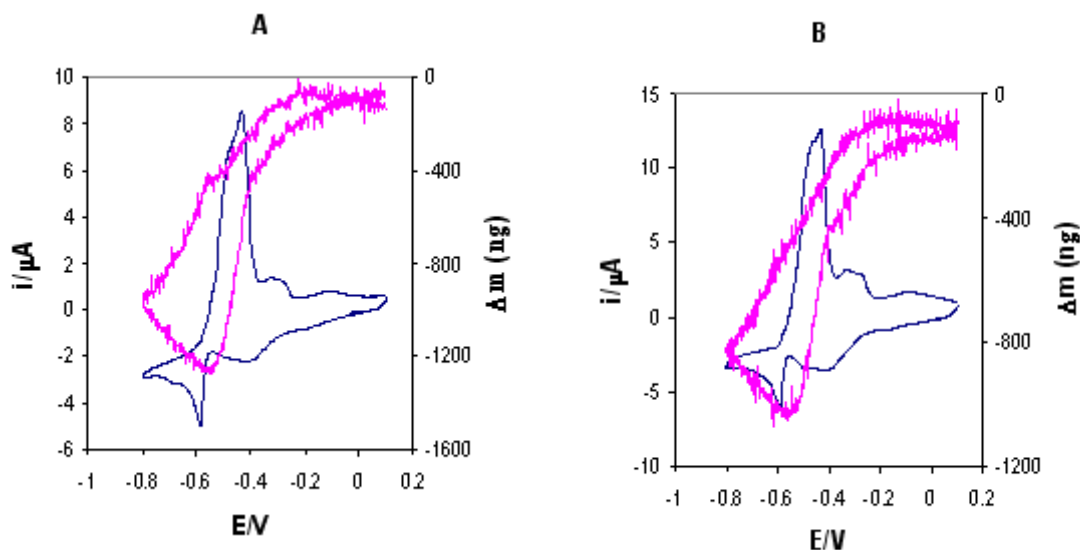
**Fig. 1: CV of 100 mM Pb²⁺ in 10 mM KCl, 1 mM HNO₃ at a bare gold electrode (thin line).
Δm (ng) results (thick line). (A) Scan rate 5 mV s⁻¹ and (B) Scan rate 10 mVs⁻¹.
The solution was bubbled with N₂ for 20 min prior to experiments.**

increase) was also observed during the stripping of the underpotential deposit. The stripping peak exhibited a shoulder, correlating with the results of other research groups that observed using polycrystalline gold electrodes[14]. Studies of Pb²⁺ potential deposation by CV were carried out at bare gold electrodes and at electrodes modified with MBA and DMPS (Fig. 2). The behaviour of the Pb potential deposation and stripping varied from one type electrode to another. At modified electrodes, the cathodic pre-peak shoulder was shifted to more negative potentials, as was the deposition peak for Pb²⁺ UPD. However, stripping peaks at the different electrode surfaces were all observed at similar potentials.

Repetitive potentiodynamic cycling led to similar CV shapes for the MBA modified electrodes and the bare gold electrode (Fig. 2B). After only three cycles CVs at the bare gold electrode and at the MBA modified electrode were practically identical. The UPD peaks were observed at the same potentials. Moreover, the shapes of the stripping peaks were very similar. The change of the voltammogram shape, after repetitive cycling, at the MBA modified gold electrode clearly demonstrated the instability of the MBA

disorganised monolayer in the potential range reign investigated. However, at the DMPS modified electrode, the Pb UPD-SV behaviour was very different after repetitive cycling (Fig. 2B) when compared with the bare gold electrode. The repetitive cycling on the DMPS modified gold electrode made the surface inactive and became de-activated.

Correlation between CV and EQCM data

The data extracted from the CVs and from the EQCM frequency change were compared, in order to gather information concerning the stability of the MBA and DMBS monolayers adsorbed on gold and their influence on the Pb UPD-SV process. During EQCM experiments when a CV is run, D*f* values are measured at the electrode surface. Sauerbrey's equation (Eq.1) allows conversion of the D*f* at the electrode surface to mass change, Dm using Farady's law[13] a linear relationship between charge, Q and mass changes can be established (Eq.2).

$$\Delta m = -Q\left[\frac{\Delta m_{pb}}{zF}\right] \quad ...(2)$$

Where M_{pb} is the atomic mass, z is the ion valency and F is Farady·s constant. By plotting mass change various the charge. It is possible to calculate the mass changes per mole of electrons, given by the slope $\Delta m/Q$. The values calculated for the different electrodes considered in this work are given in Table 1.

The values presented in Table 1 were obtained using the deposition process in the potential range between -0.28 V and -0.8 V. The values calculated at the different electrodes were much lower than the theoretical value of 103.6 g mol^{-1} (207.2/2 = 103.6 g mol^{-1}). These results indicate Pb^{2+} UPD is accompanied by a process

that involves a mass change at the electrode surface in opposition to that occurring during UPD (i.e. loss of mass from the electrode surface). Similar results were obtained by Henderson et al. when Pb UPD-SV was studied in perchloric acid solution[16]. Using EQCM combined with a probe beam deflection study enabled the distinction of three stages in the Pb UPD. The first step was the ejection of water from the Au surface. The Pb UPD was accompanied by the reaction of hydroxide adsorbed on the electrode surface to form water. These opposing transfers of mass could be responsible for the low values obtained. The values obtained in the present study were lower than the value measured by Henderson *et al.*[16], indicating that species other than
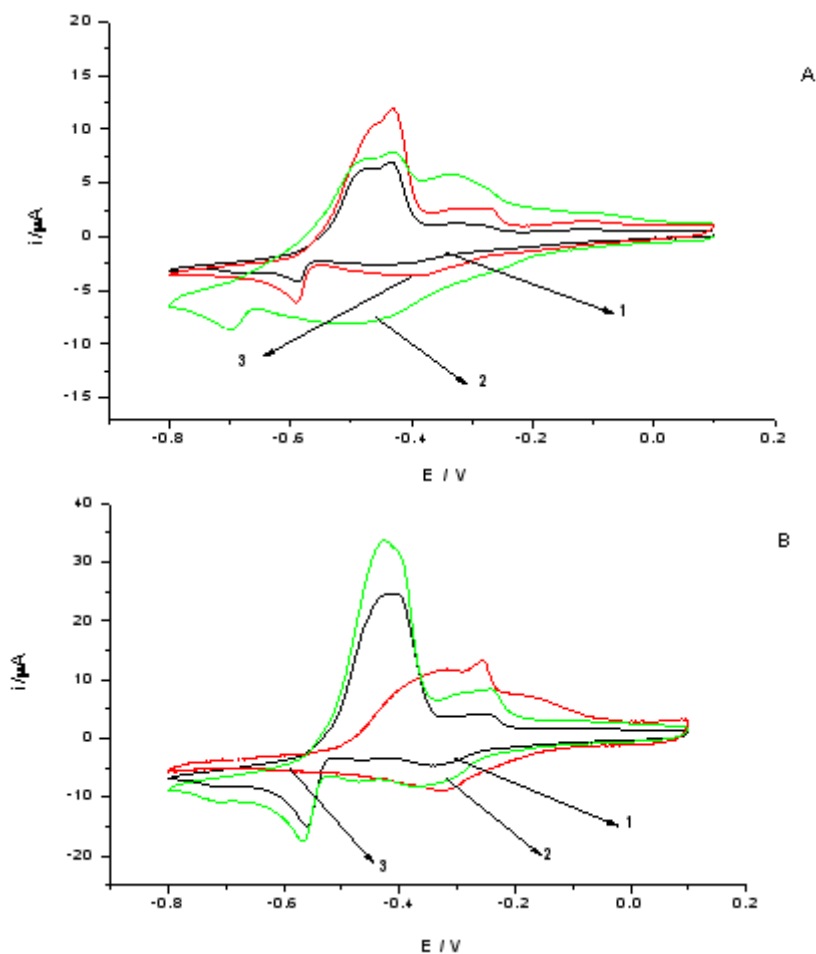

Fig. 2. CV of 100 mM Pb^{2+} in 10 mM KCl, 1 mM HNO$_3$ at a bare gold electrode (1), at a MBA modified gold electrode (2) and at DMPS modified gold electrode (3). (A) First cycle, (B) Third cycle. The solution was bubbled with N$_2$ for 20 min prior to experiments. V = 10 mVS^{-1}

Table 1: Mass changes per mole electron at the different electrodes studied. Values calculated for the deposition process between -0.40 and -0.65 V. Same experimental conditions as Fig.4

Electrode	Mass change per mole electron / g mol^{-1}
Bare[a]	10.4
MBA –modified[b]	7.3 (1st cycle)
	9.3 (2nd cycle)
	9.8 (3rd cycle)
DMPS-modified[a]	11.2

water and adsorbed hydroxide are responsible for the mass loss. Their experiments were done in the presence of perchlorate anions, a species that does not adsorb on gold under the selected experimental conditions, unlike chloride or nitrate[17], the anions selected for the present study. The implication of those studies[16-17] for the present report is that up to four species other than Pb^{2+} might also be responsible for the difference between the theoretical value and the experimental values of the mass change per mole of electrons (Δm/Q): chloride and nitrate anions, anionic lead complexes as suggested in[18]. As seen previously for the Pb UPD, the mass change per mole electron should
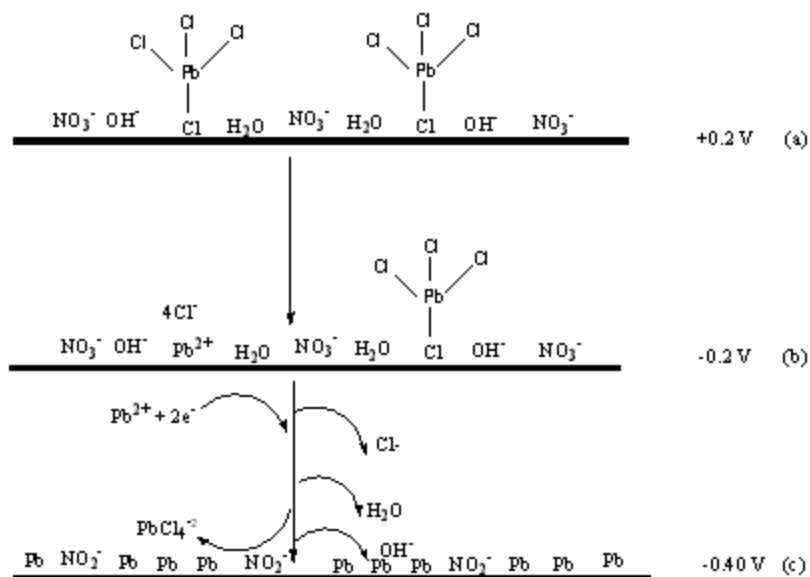

Fig. 3: Proposed mechanism for the deposition of Pb UPD at a bare gold electrode surface

theoretically be 103.6 g mol^{-1} . Fig.3 shows explanation of the electrochemical process taking place at the bare gold electrode surface. This schematic takes into account both studies of Henderson et al.[16] and Zeng and Bruckenstein[18].

At the beginning of the potential scan four species are believed to be adsorbed on the electrode surface: water molecules, hydroxide, nitrate and lead chloride complexes. The concentration of Cl- in the solution can lead of the formation of [PbCl$_4$]$^{-2}$ complexes[18]. The reduction of

the adsorbed [PbCl$_4$]$^{-2}$ to Pb UPD during the negative direction scan in the potential region between -0.25 and -0.42 V was investigated.

$$\left[PbCl_4\right]^{-2} + 2e - \rightarrow Pb\ UPD + 4Cl^- \quad ...(3)$$
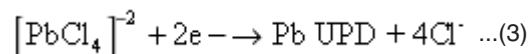
The stability of the Δf values in this region (Figure 1) suggests that chloride ions remain adsorbed on the electrode surface until the start of the UPD process. The Pb UPD at -0.45 V is accompanied by the desorption of water and

hydroxide, and reduction of nitrates to nitrites according to equation 5.

$$H^+ + e^- + NO_3^- \rightarrow NO_2^- + \tfrac{1}{2}H_2O \quad ...(4)$$
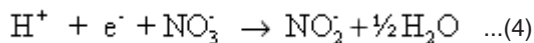
This reaction is possible at underpotentially deposited lead atoms. Desorption of chloride and water is responsible for mass changes per mole electrons (corresponding to equations 4 and 5) of 71 and 16 g mol^{-1}, respectively. Pb UPD, as seen
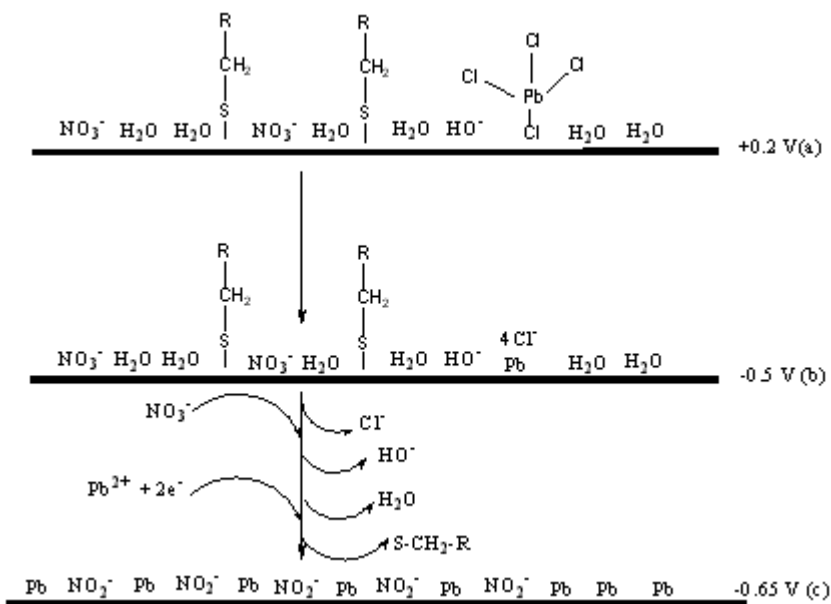

Fig. 4: Proposed mechanism for the Pb UPD at MBA and DMPS modified gold electrodes

earlier, results in the mass change per mole of electron of 103 g mol^{-1} . The overall mass change per mole of electrons (for the complete process involving Pb UPD plus equations 4 and 5) is 16.6 g mol-1 which is close to the value of 10.6 g mol^{-1} obtained experimentally (Table1).

A proposed mechanism for the Pb UPD process at the thiol-modified electrodes is shown in Figure 4. At these electrodes, the adsorption of the anions as proposed by Zeng and Bruckenstein[18-19] would be limited, since under these experimental conditions DMPS was negatively

Table 2: Surface coverage and stripping peak charge density
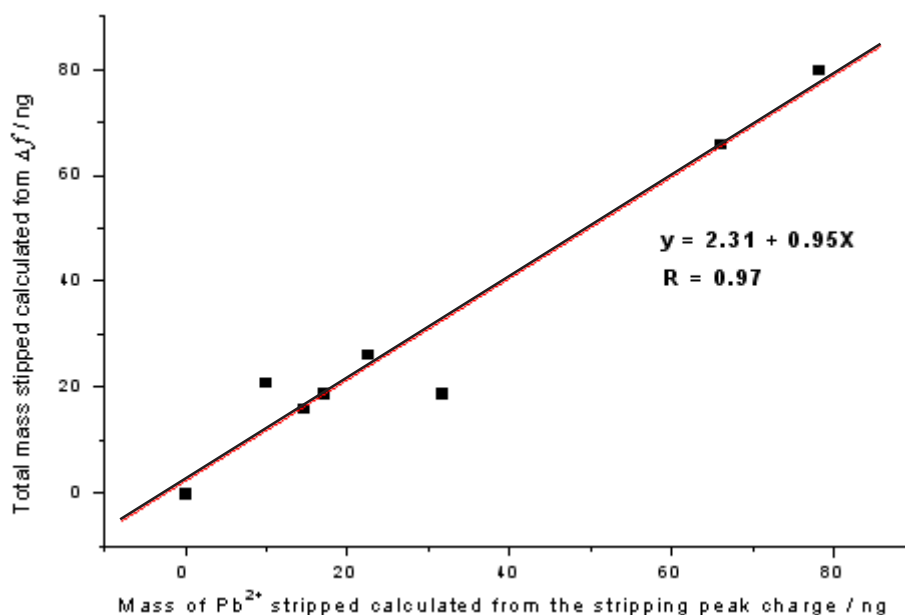**obtained from the CV. same experimental conditions as Fig. 4.**

Electrode	Γ/ mol cm^{-2}	Q / µC cm^{-2} Experimental values	Q / µC cm^{-2} Literature value
Bare[a]	6.8×10^{-10}	181	420 [13]
	1.09×10^{-9}	205	
MBA-modified[b]	9.02×10^{-10}	177	Data not available
DMPS-modified[a]	1.02×10^{-9}	199	Data not available

[a] The value given was calculated using the first CV.

[b] The values given were calculated for three consecutive CVs.

charged whereas the MBA monolayer perhaps be present in equilibrium between carboxylic acid and carboxylate terminating groups (solution pH =3; pKa of the carboxylic acid group = 4.5[20-21]. At +0.20 V, the electrode surface unoccupied by thiol molecules would be occupied mainly by adsorbed molecules of water but also nitrate, hydroxide and lead chloride complexes. It is believed that these electrons rich and voluminous complexes would be adsorbed to

some extent on the (even party) negatively charged modified electrodes. Indeed, the cathodic shoulder at -0.40 V (Fig. 2) suggests that these complexes are present and that the Pb(II) species are reduced to underpotentially deposited Pb. At the modified electrodes, the potential is shifted to more negative potentials due to the presence of the thiols (Fig. 2). At -0.65 V, four species are believed to leave the electrode surface: water molecules, hydroxide,

Fig. 5: Correlation plot between the masses obtained by CV and EQCM studies (stripping values). Same experimental conditions as Fig. 2

chlorides and thiolates, all of them adsorbed on the surface, plus water molecules that result from the reduction of nitrates (Eq.4).

The theoretical total mass change (i.e. the sum of all mass changes for all species believed to be involved in the electrode reaction) per mole of electrons for all the species involving the electrode surface is -250 and -300 g mol^{-1}, for DMPS and MBA modified electrode respectively. On the other hand, two species contributes to the increase of mass change per mole of electrons: underpotentially deposited Pb^{2+} (103.6 g mol^{-1}) and nitrate, from the solution, which is adsorbed and reduced (46 g mol^{-1}). The overall mass changes per mole of electrons for the whole process (adsorptions and

desorptions combined) are -50.4 and -100.4 g mol^{-1} for DMPS and MBA modified electrodes, respectively, in principle. These values are a lot lower than the ones measured experimentally (table1) indicating that other processes occur at the modified electrode.

The stripping processes

Using Faraday,s law (Eq. 2), the mass of Pb^{2+} stripped from the surface of the electrode is calculated from the voltammetric peak charge. The values obtained at each of the electrode types are compared in Fig. 5 with the mass change extracted from Δf, using Sauerbrey,s equation (Eq. 1). A general trend (Fig. 5) is observed, with the values calculated from Δf increasing with those calculated

from the stripping charge; however the former are greater than the latter. This implies that other species leave or added to the electrode surface during the stripping process. These species could be stripping of co-deposited anions or the re-adsorption of thiols on the surface.

The surface coverage and the peak charge densities for the Pb monolayer obtained from this work are compared to theoretical $(2.0 \times 10^{-9}$ mol cm^{-2})[22] or experimental values obtained by others in Table 2. The surface coverage at the different electrodes studied were below the theoretical value. Furthermore, at the bare gold electrode, the peak charge density calculated is lower than that measured in 0.5M KCl.

CONCLUSIONS

Attempts to extend the disorganised monolayer approach to other substrate or target analytes were not successful. The major drawback is the overlapping of the thiol reductive desorption peak and the UPD of Pb. From the present studies concerning both deposition and stripping processes, it appears that the monolayer of thiols was adsorbed during Pb UPD-experiments. However, the complexity of the system investigated did not allow a full understanding of the processes occurring. We note however that in the studies by Shen et al[23-24], who employed thiol-self-assembled monolayers on gold electrodes for the stripping voltammetry of Pb that did not observe any reductive desorption of the thiol. Under the conditions of the UPD-SV employed in this work, the reductive desorption processes of the thiol monolayer occur in similar potential regions, making analytical applications impossible. Further experimental investigations will be required for a full understanding of these different reactions.

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