# An EQCM-D study of the influence of chloride on the lead anodic oxidation

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## ARTICLE INFO

## ABSTRACT

The influence of chloride on the electrodeposition of lead films and their dissolution in anodic stripping voltammetric experiments was examined. Gold substrates were plated with lead films, and mass changes were monitored by using the electrochemical quartz crystal microbalance with dissipation factor (EQCM-D). The results showed that the amount of electrodeposited lead is slightly dependent on the chloride concentration. The charge/mass ratio data indicated the presence of Pb(I) and Pb(II) as a result of film dissolution, and the precipitation and deposition of $PbCl_2$ onto the electrode surface. Scanning electron microscopy images revealed that the morphology of the lead film was strongly influenced by chloride present in the plating solution and that much rougher films were obtained in comparison with those obtained in the absence of chloride. The rate of the anodic dissolution was higher for lead films with higher surface areas, which lead to an increase in their stripping voltammetric currents.

## 1. Introduction

Electroanalytical methods for metal determination often require a preconcentration step in order to detect the analyte at very low concentrations. Mercury is the most commonly used electrode for such analyses in stripping voltammetry techniques [1–3], mainly due to the high hydrogen overvoltage and the ability of mercury to form amalgams with several metals. However, since mercury is a toxic metal, other materials such as bismuth and antimony have been used in stripping analyses [4–9]. The accumulation of the analyte can also be done directly at bare surfaces and the literature reports the use of carbon [10–12] and gold electrodes [13,14].

The electrochemical quartz crystal microbalance (EQCM) technique is widely used for measuring the change in the mass of an electrode while a film is deposited on or stripped off from the electrode surface. When an EQCM with dissipation (EQCM-D) is used, the recording of resonance frequencies of the electrode and the dissipation of a film during its electrodeposition or dissolution can provide certain information, *e.g.*, about the mechanism by which the deposition or the dissolution occurs, deposition/dissolution efficiency (based on charge/mass ratio), and viscoelastic properties [15–18].

Several studies for analyzing the electrodeposition of lead onto different substrates by using the EQCM or EQCM-D have been performed by focusing, for instance, on the underpotential deposition [17,19–21] and the effect of other substances, such as oxygen, sulfur, bismuth, and copper on the film deposition [16,22–24].

The determination of lead by stripping analysis using gold as a substrate has been reported in the literature [14,25–31]. In some reports, the influence of chloride on the lead electrodeposition has been described, [14,31,32] but to the best of our knowledge, this influence has not been extensively investigated and characterized. The use of EQCM-D and scanning electron microscopy (SEM) facilitated a better understanding of this phenomenon by showing clearly the influence of chloride anions on the deposition and dissolution processes. This understanding is very important in evaluating the influence of sample composition on the electroanalytical determination of Pb(II) and in ensuring reliable analysis.

## 2. Experimental

### 2.1. Reagents

All reagents were of analytical grade and used without any further purification. $Pb(NO_3)_2$, KCl, and $K_3[Fe(CN)_6]$ solutions were prepared by dissolving the reagents in deionized water processed through a water purification system ($18.0\,M\,\Omega\,cm^{-1}$, Nanopure Infinity, Barnstead, Iowa, USA). The nitric acid solution was prepared by diluting the stock solution, as necessary. All reagents were obtained from Merck (Darmstadt, Germany).

### 2.2. Square wave voltammetry experiments

An Autolab PGSTAT 30 (Eco Chemie) was used for experiments with square wave voltammetry (SWV), a technique that has been

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largely used to improve the sensitivity of analytical determinations [33]. A gold disc microelectrode was used as the working electrode for the stripping analysis. A homemade Ag/AgCl$_{(sat. KCl)}$ electrode, inserted in a separate compartment to avoid chloride contamination, and a platinum wire were used as reference and counter electrodes, respectively. Before each experiment, a positive potential ($E_{cleaning}$ = 0.70 V) was applied to the electrode for 2 min ($t_{cleaning}$ = 120 s). Lead was then deposited at the microelectrode surface ($E_{deposition}$ = −0.70 V) in solutions containing 0.1% (m/v) HNO$_3$, 0.1 µmol L$^{-1}$ Pb$^{2+}$ with different chloride concentrations (in the range 0–50 mmol L$^{-1}$). Lead was stripped off by SWV at the same solution employed in the deposition step. The potential was scanned from −0.70 to 0.10 V and the potential step ($E_{step}$), potential amplitude ($E_{amplitude}$) and frequency parameters were 5 mV, 25 mV and 300 Hz, respectively.

The gold microelectrode was fabricated as follows: a gold fiber (diameter = 25 µm, Goodfellow Cambridge Ltd., Cambridge, England) was connected to a Ni/Cr wire with silver ink conductive paint (Joint Metal Comércio Ltda, São Paulo, Brazil), and then inserted into a glass capillary and flame-fuse sealed in the tip of the glass capillary. The radius of the working microelectrode was determined by measuring the steady-state current in a K$_3$[Fe(CN)$_6$] solution of known concentration, and the value was found to be 12.5 µm.

### 2.3. Scanning electron microscopy experiments

A scanning electron microscope (FESEM JSM-7401F, JEOL) using a LEI detector, 1.0 kV accelerating voltage and 8 mm working distance was used for image acquisition of different lead films electrodeposited onto gold microfibers ($r$ = 63 µm). Electrodeposition for 480 s was accomplished at −0.70 V using solutions containing 0.1% (m/v) HNO$_3$ and 0.1 µmol L$^{-1}$ Pb$^{2+}$, with different chloride concentrations (in the range 0–75 mmol L$^{-1}$).

### 2.4. Electrochemical quartz crystal microbalance with dissipation experiments

The EQCM-D measurements were carried out with a QCM-D system from Q-Sense (Göteborg, Sweden) and an Autolab PGSTAT 30 (Eco Chemie, The Netherlands), by simultaneously monitoring the changes in resonance frequency ($\Delta f$), dissipation ($\Delta D$) and current. The change in $\Delta f$ can be related to the change in mass ($\Delta m$) in the case of a rigid film by using the Sauerbrey equation (1) [34]:

$$-\Delta f_n = \left(\frac{C}{n}\right) \Delta m \tag{1}$$

where the mass sensitivity $C$ was 17.7 ng cm$^{-2}$ Hz$^{-1}$ and $n$ is the overtone (1, 3, 5, 7, 9, 11, and 13). A gold electrode (Q-Sense) was used as the working electrode after cleaning it with an alkaline piranha solution (1:1:5 H$_2$O$_2$/NH$_4$OH/H$_2$O mixture at 70 °C) for 5 min. The electrode was then rinsed with deionized water, sonicated for 5 min in deionized water and ethanol, dried with a nitrogen stream, and then kept in a UV/Ozone cleaner (ProCleaner Plus BioForce) for 15 min prior to use. A Pt spiral wire and a homemade Ag/AgCl$_{(sat. KCl)}$, which was inserted in another compartment to avoid chloride contamination, were employed as counter and reference electrodes, respectively.

The studies regarding the film deposition (at −0.70 V) were performed in solutions containing 0.1% (m/v) HNO$_3$ and 5 mmol L$^{-1}$ Pb$^{2+}$ with different chloride concentrations (in the range 0–75 mmol L$^{-1}$). In order to examine the film dissolution, the electrodeposition was carried out at potentiostatic conditions (−0.70 V) in solutions containing 0.1% (m/v) HNO$_3$, 5 mmol L$^{-1}$ Pb$^{2+}$ and different chloride concentrations (in the range 0–75 mmol L$^{-1}$). Then, the film was stripped off using linear sweep voltammetry (LSV) from −0.70 to 0.70 V at different scan rates (from 1 to
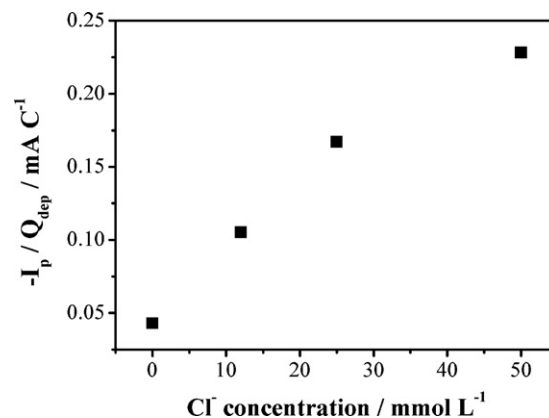


**Fig. 1.** Stripping peak current/charge deposition as a function of Cl$^-$ concentration. Lead analysis performed using square wave voltammetry on a gold microelectrode ($r$ = 12.5 µm) with solutions containing 0.1% (m/v) HNO$_3$, 0.1 µmol L$^{-1}$ Pb$^{2+}$ and varying Cl$^-$ concentrations (12.5, 25 and 50 mmol L$^{-1}$) in a quiescent solution. Parameters used: $E_{cleaning}$: 0.70 V, $t_{cleaning}$: 120 s, $E_{deposition}$: −0.70 V, $t_{deposition}$: 480 s, $E_{final}$: 0.10 V, Frequency: 300 Hz, $E_{step}$: 5 mV, $E_{amplitude}$: 25 mV, $t_{equilibrium}$: 10 s.

100 mV s$^{-1}$). Experiments involving film dissolution were performed using solutions containing 0.1% (m/v) HNO$_3$ and different concentrations of chloride and Pb$^{2+}$. As in the deposition step, chloride concentrations were in the range of 0–75 mmol L$^{-1}$. Pb$^{2+}$ was mainly at a concentration equal to 5 mmol L$^{-1}$ unless in one of the experiments, where a free lead solution was used. At this experiment, a peristaltic pump (Gilson MINIPULS Evolution, France) was used to slowly exchange the deposition solution from the dissolution solution.

## 3. Results and discussion

### 3.1. Square wave voltammetry experiments

Preliminary experiments were carried out to confirm the influence of chloride on the lead stripping voltammetric oxidation peak. Data were obtained by square wave voltammetry, as described in the experimental section, using a gold microelectrode in solutions containing 0.1% (m/v) HNO$_3$ and 0.1 µmol L$^{-1}$ Pb$^{2+}$ in the presence of different chloride concentrations (range of 0–50 mmol L$^{-1}$). Fig. 1 shows the ratio of the peak current ($E_{peak}$ = 0.10 V) recorded during the stripping step to the charge associated with the lead electrodeposition process, under each experimental condition. Since the SWV current was normalized by the charge (typical values ranged between −20 and −30 µC), the increase in this ratio as a function of the chloride concentration confirms the significant influence of the halide on the stripping response, as already reported in the literature [14,31,32].

### 3.2. Effect of chloride on film deposition

The influence of chloride on the electrodeposited lead film was firstly studied by scanning electronic microscopy (SEM). Images of the gold surface were taken after lead electrodeposition performed in the absence and presence of 25, 50, and 75 mmol L$^{-1}$ chloride under potentiostatic conditions ($E$ = −0.70 V). In the absence of chloride, a flat surface was obtained (Fig. 2(A)), whereas much rougher surfaces were seen when the lead was plated in solutions containing chloride (Fig. 2 (B–D)). These results clearly demonstrate the influence of chloride on the morphology of the electrodeposited lead film. Jones et al. reported that differences in stripping voltammetry can be explained by the differences in the orientation and morphology of the deposited film, since the surface structure can affect the stripping process [35].