Underpotential Deposition and Adsorption of Lead on Gold Polycrystalline Electrodes

II. EQCM Investigation in Acidic 0.1 M NaClO₄ and 0.1 M NaCl Electrolytes

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We describe an approach that leads to a mechanism describing the lead ion adsorption and lead underpotential deposition (UPD) on a polycrystalline gold electrode in supporting electrolytes containing chloride, nitrate and/or perchlorate. By combining the electrochemical quartz crystal microbalance (EQCM) method with data from X-ray photoelectron spectroscopy and time of flight secondary ion mass spectrometry, the existence of adsorbed anionic ligands was demonstrated. The lead UPD process goes through the reduction of both an adsorbed lead complex and a lead species present in the supporting electrolyte.

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Adzic et al.,¹ Schultz and Dickerman,² Engelmann and Lorenz,³ and Hamelink and Lipkowski, et al.⁴ investigated the underpotential deposition (UPD) of lead on single crystal and/or evaporated gold electrodes in perchloric acid solution. Because these workers’ studies showed that perchlorate was only weakly adsorbed at a gold electrode, we thought that it would be a good model system to which additional studies involving lead ion adsorption could be compared. Consequently, this system was reinvestigated to aid a study of the processes leading to UPD lead formation at a gold electrode from a chloride medium.

UPD of lead at a gold electrode has been studied by various authors. Timmer et al.⁵ used impedance analysis in the potential region of the faradaic reaction, and Caselli and Papoff⁶ applied chronocoulometry. Barclay and Anson⁷ used chronocoulometry, and Gewirth et al.⁸ studied structural properties of the catalytically active phase of UPD lead on Au(111) by atomic force microscopy. Green and Hanson⁹ studied alloy formation of lead on a gold electrode by scanning tunneling microscopy, and Vicente and Bruckenstein¹⁰ studied lead UPD with the rotating ring-disk electrode (RRDE).

Vicente and Bruckenstein¹⁰ found that the UPD of Pb(0) on a gold electrode occurred at 0.0 V > E > −0.6 V vs. saturated calomel electrode (SCE) in 0.1 M slightly acidic KCl medium. The adsorption of Pb(II) on the gold electrode began at about +0.6 V during the negative potential scan of the disk. They showed that an adsorbed lead species, possibly an adsorbed chloro complex, existed at the gold electrode at potentials just before the UPD discharge region.

Adsorption of lead ions on gold from chloride solutions is of great interest because Pb(II) complexes containing more than one chloride ion are difficult to form in 0.1 M chloride aqueous solutions.¹¹ Under these conditions, the principal lead species are the aquo- and monochloro Pb(II) ions. Surprisingly, evidence for adsorbed lead complexes exists at positive rational potentials.¹² The latter observation suggests that the adsorbed chloro complex was an anion. Also, evidence for adsorbed chloride ions at a gold electrode¹³ suggested the existence of chloride bridges between the electrode and the adsorbate. Our study extends the earlier work of Vicente and Bruckenstein.¹⁰ It disentangles the details of lead ion adsorption, anion adsorption, and desorption from the processes that accompany UPD lead formation and stripping at the gold electrode.

It also yields the stoichiometry of the adsorbed lead chloro complex. This approach used in studying the UPD lead system also serves as a model for the techniques that can successfully study adsorption of metal complexes at solid electrodes from the supporting electrolytes containing an adsorbable ligand.

A single electrochemical technique provides only limited kinetic and stoichiometric information concerning a UPD process. Some conclusions drawn about adsorbed species are made by inference. Two electrochemical techniques used in tandem can provide much more information, and strengthen the validity of inferences. Additionally, combining appropriately chosen nonelectrochemical techniques with the electrochemical methods can remove nearly all ambiguities about stoichiometric and surface speciation details. Consequently, data obtained using the electrochemical quartz crystal microbalance (EQCM) have been combined with X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (TOF-SIMS) data from Part II of this series.

The EQCM provides a unique means for determining the mass changes associated with the adsorption or desorption of a species at an electrode and for correlating these processes with charge transfer processes. Combining our new EQCM results with those of Vicente and Bruckenstein,¹⁰ RRDE data gives aggregate information about surface coverages of adsorbates. It then becomes possible to distinguish between (i) species adsorption with and without charge transfer, (ii) UPD deposition from solution or from an adsorbate, and (iii) UPD deposition from a complexed adsorbate. Adding TOF-SIMS and XPS to the EQCM experiments provides the complementary information necessary to characterize the electrochemically produced adsorbates, and thus completes the picture of the entire UPD discharge process.

Experimental

Systems Studied

Experiments were done in different chloride–containing electrolytes: 0.1 M NaCl + 10⁻⁴ M HCl or 0.1 M HCl. In the 0.1 M HCl medium, the hydrogen evolution potential was almost the same as the bulk lead deposition potential. Thus, the 0.1 M NaCl + 10⁻⁴ M HCl medium was chosen as most suitable to study the adsorption and UPD of lead on gold. Studies were also carried out in 0.1 M NaClO₄ + 10⁻⁴ M HClO₄. It was chosen as a reference system because lead is thought not to form complexes with perchlorate ions, and perchlorate ions are only weakly adsorbed on a gold electrode.

Reagents

All chemical used were of reagent quality. Both reagent grade Pb(NO₃)₂ and Pb(NO₃)₃ were used. Stock solutions of 0.1 M Pb(NO₃)₂ or 0.1 M Pb(NO₃)₃ were diluted with supporting electrolyte (0.1 M NaCl + 10⁻⁴ M HCl) to make different concentrations of Pb(II) solutions. Water was prepared from a four-column Millipore system with a terminal 0.22 μm filter.

Equipment

An operational amplifier-based potentiostat, in which the working electrode was at virtual ground, was used. All potentials report-

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ed in this work are reported vs. the SCE. The EQCM apparatus used in this work has been described elsewhere.14

**Electrode Pretreatment**

Before each measurement, the gold electrode of the EQCM crystal was cleaned with a fresh 1:1 mixture of concentrated H₂SO₄ and HNO₃. Then, its potential was cycled several times in 0.2 M HClO₄ between the potentials that yielded a gold oxidation current and hydrogen discharge reduction current. This procedure produced voltammograms characteristic of a clean gold surface. Our experience with this approach showed that, after this pretreatment, the evaporated gold electrodes on the 10 MHz EQCM quartz crystals that were used had same roughness factors within a few percent. Then, the electrode was transferred to 0.1 M NaCl or 0.1 M NaClO₄ electrolyte. Next, either a small volume of a stock solution containing Pb(NO₃)₂ or Pb(ClO₄)₂ was injected to make the Pb(II) concentration 7.7 mM in the supporting electrolyte.

**Results and Discussion**

**Current and Mass Dependence on Electrode Potential and the Supporting Electrolyte: 0.1 M NaClO₄ or 0.1 M NaCl electrolyte.**

Figure 1a and c gives the cyclic current potential (I-E) (curve a) and mass potential (Δm-E) (curve c) plots obtained at an EQCM gold electrode in Pb(II)-free 0.1 M NaClO₄ or 0.1 M NaCl electrolytes. The gold electrode was conditioned at +0.3 V for 1 min before scanning the electrode potential at 50 mV/s. The I-E curve is unremarkable. The Δm-E curve shows no mass change in the potential region between +0.3 and 0.0 V where the rational potential is positive. (The point of zero charge, PZC, of gold is ~0.04 V.15) The mass increases slightly at 0 V during the negative-going potential scan and decreases when the scan was reversed at ~0.4 V. This behavior can be rationalized by adsorption and desorption of Na⁺ when the rational potential becomes negative or positive16 during the negative- and positive-going potential scans, respectively.

EQCM I-E and Δm-E curves for a gold electrode in 0.1 M NaCl or 0.1 M NaClO₄ electrolyte free of Pb(II) are presented in Fig. 1b and d. The electrode was conditioned at +0.3 V for 1 min and then the potential was scanned at a rate of 50 mV/s to more negative potentials. During the negative-going potential scan, the mass decreases because Cl⁻ desorbs, but at ~0.1 V, the mass increases slightly due to Na⁺ adsorption. During the reverse scan, the mass decreases between ~0.4 and 0 V because Na⁺ desorbs, and then increases after 0 V because Cl⁻ adsorbs. The minimum change of mass at ~0.0 V was in the potential region of the PZC of Au. The I-E curves also showed corresponding small Cl⁻ desorption and adsorption peaks arising from double layer processes.

**Adsorption and UPD Studies**

The interpretation of the various steps associated with reduction and oxidation in the various supporting electrolytes is complicated.
Note the proposed mechanisms in Fig. 2 ( perchlorate electrolyte), Fig. 3 (chloride electrolyte 15.4 mM perchlorate ions), and Fig. 4 (chloride electrolyte 15.4 mM nitrate ions). In subsequent sections, evidence is provided to support each step given in these three figures.

Pb(II) injection experiments into ClO₄⁻ or Cl⁻ media.—A volume of 0.1 M lead nitrate or lead perchlorate solution was injected into the cell containing 0.1 M NaClO₄ + 10⁻⁴ M HClO₄ or 0.1 M NaCl + 10⁻⁴ M HCl supporting electrolyte while keeping the electrode potentiostated at \( E = 0.3 \) V. The volume was chosen to raise the Pb(II) concentration to 7.7 × 10⁻³ M. Experiments show that no mass increase (Fig. 5a) or charge consumption occurs when lead perchlorate is injected into 0.1 M NaClO₄ + 10⁻⁴ M HClO₄. However, as seen in Fig. 5b, an electrode mass increase of 9.5 ng occurred when Pb(NO₃)₂ was injected in the 0.1 M NaClO₄ + 10⁻⁴ M HClO₄ electrolyte. No current passed during and after injection of the Pb(II) solution. This mass increase was mainly due to NO₃⁻ adsorption caused by injecting the lead nitrate solution.

As shown in Fig. 5c and d, at \( E = +0.3 \) V, the adsorption of some species without charge transfer occurred on the injecting lead nitrate or lead perchlorate solutions into the 0.1 M NaCl + 10⁻⁴ M HCl supporting electrolyte. These experiments show that no lead species is adsorbed at the gold electrode unless chloride ions are present in solution. It also shows that the mass increase is 15 ng more when lead nitrate solution was used (Fig. 5d) than when lead perchlorate was used (Fig. 5c) in the chloride-containing electrolyte. This extra mass increase is caused by the nitrate adsorption.

As shown in Part I of this series, at \( E = 0.3 \) V, the adsorbed Pb(II) is an anionic lead complex. Moreover, since anionic lead chloride complexes are virtually absent in the supporting electrolyte whose concentration of chloride ions is only 0.1 M and one chloride was originally adsorbed on the surface before injection, the adsorption process is described as

\[
\text{Pb(II)} + 3\text{Cl}^-_{\text{soln}} + \text{Cl}^-_{\text{ads}} \rightarrow \text{PbCl}_2^{2-} + \text{Au} \quad [1]
\]

Eq. 1 suggests that adsorbed chloride ion induces the adsorption of Pb(II), through a ligand (chloride ion) bridge.

No changes in the electrode mass and current were observed at \( E = +0.3 \) V on doubling the Pb(II) concentration by a second injection of the same Pb(II) solution. Also the \( D_m-t \) curves at two different Pb(II) concentrations, 7.7 mM (first injection) and 14.3 mM (second injection) were identical. Thus, saturation coverage of Pb(II) adsorption was achieved in 7.7 mM Pb(II) solution.

Current-voltage curves of Pb(II) UPD in Cl⁻ and ClO₄⁻ media.—Figure 6a-c are the current voltage curves for 7.7 mM Pb(ClO₄)₂ or 7.7 mM Pb(NO₃)₂ adsorption and UPD processes in an acidic sodium perchlorate medium and an acidic sodium chloride medium. In the negative potential scan, the two peaks, B and C, seen in perchlorate solutions (Fig. 6a) merge into one peak (peak H) in the negative potential scan of the chloride solutions (Fig. 6b) at \( E = 0.3 \) V.
forms at H in chloride medium and peaks A, B, and C in perchlorate medium from chloride solutions (Fig. 6b and c). Also, peaks D, E, and F in chloride media are absent in perchlorate solutions. All these peaks occur before bulk lead deposition in these media. As shown below, peaks D, E, and F arise from chloride desorption, and peaks G and H in chloride medium and peaks A, B, and C in perchlorate medium arise from lead UPD. The peak potentials for UPD lead deposition are more negative in chloride medium as compared with perchlorate medium. This occurs for three reasons. First, as XPS studies show in Part I, a species with the stoichiometry of an adsorbed PbCl₄²⁻ forms at +0.3 V; this adsorbate may block the reduction of the dissolved aquo lead ion. Second, because of thermodynamics, complexed adsorbates can be reduced only at a more negative potential than noncomplexed adsorbates. Third, the specific strong adsorption of an anion, such as chloride, shifts metal UPD peaks to more negative potentials.

In acidic sodium chloride medium, introducing millimolar nitrate also causes the cathodic peak potentials to shift to more negative potential as is seen in Fig. 6c. We postulate in Part II that this is caused by adsorption and reduction of some nitrate to adsorbed nitrite.

**Scan rate effects accompanying the Pb UPD process in Cl⁻ and ClO₄⁻ media.**—Both in a chloride medium and a perchlorate medium, UPD of lead produces multiple current peaks at the gold electrode. We set out to decide whether these peaks arise from a diffusion- or surface-controlled process, or a combination of these two possibilities. As discussed elsewhere, this issue can be decided by plotting \( i_{p}^{1/2} \) vs. \( v^{1/2} \). This plot will be linear for both cases. The plot intercept is directly related to the diffusion process, while its slope relates to the surface process. A zero slope signifies a pure diffusion-controlled process, a zero intercept signifies a pure surface-controlled process, and a nonzero slope and intercept signifies a process in which both diffusion and surface control are important.

**Perchlorate medium.**—In perchlorate medium, cathodic peaks A and C and the sum of anodic peaks B' and C' do not show the behavior of a diffusion-controlled process. Rather they appear to be a mixture of surface and diffusion control processes (nonzero slopes and intercepts in Fig. 7). The XPS data in Part I also show the existence of a Pb-containing adsorbate on an Au electrode emersed in the potential range of the peak current used in the plot of Fig. 7. We suggest that deviations from linearity are caused by kinetically controlled processes and we rationalize the origin of the cathodic process producing peak C as involving an adsorbate formed in the potential region of peak A. Peak A', with a zero intercept, is a pure surface process. These conclusions agree with the XPS data presented in Part I. We believe that the deviations from linearity in the \( i_{p}^{1/2} \) vs. \( v^{1/2} \) plots are caused by kinetically controlled processes.

**Chloride medium.**—Figure 8 gives the \( i_{p}^{1/2} \) vs. \( v^{1/2} \) plots for the various cathodic and anodic peaks of 7.7 mM Pb(II) in chloride medium. The cathodic peaks G and H, and the anodic peak J are the result of a mixture of both diffusion and surface processes that contribute to the total current to similar extent. The zero intercepts of \( i_{p}^{1/2} \) vs. \( v^{1/2} \) curves of anodic stripping peaks I and G' in Fig. 6c show that they are caused by a pure surface-controlled process. It precedes the diffusion of lead ions from the electrode to the bulk of solution. The nonlinearity of \( i_{p}^{1/2} \) vs. \( v^{1/2} \) plots for peaks H, I, and G' probably are caused by kinetic complications. These arise from the changing surface concentration of chloride caused by its adsorption or desorption during anodic peaks H, I, and G' potential regions.

**Mechanisms of lead UPD in chloride and perchlorate media.**—

Cathodic reduction mechanism in acidic sodium perchlorate medium.—Figure 9a shows the simultaneously recorded mass-charge (Δm-Q) curve corresponding to the I-E curves in Fig. 6a obtained at a voltage scan rate 200 mV/s in perchlorate medium containing 7.7 × 10⁻³ mol/L Pb(NO₃)₂. During the cathodic scan, the mass changed almost linearly with the charge between +0.2 and −0.31 V, i.e., at the foot of the final cathodic peak. Between −0.31 and −0.41 V, the charge increased with almost no mass change, which also is seen in Fig. 10a. This probably was caused by the reduction of some adsorbed NO₃⁻ to adsorbed NO₂⁻.

As seen in Fig. 9a, there are two similar slopes (A’B’ and B’E’) in the cathodic and the anodic portions of the Δm-Q plot in the potential range between +0.3 and −0.4 V. As seen in Fig. 6a, this is the potential region of UPD lead formation (peaks A, B, and C) and stripping (peak A’, B’, and C’). The average of the values of two slopes, \( Δm/Q \), gives a molar mass of 209 g/mol for the UPD species, close to that of lead, 207.2 g/mol. This results shows that the redox processes causing these peaks involve the same species, UPD lead. We note that linear \( Δm/Q \) plots give limited information about the underlying processes causing the cathodic and anodic Δm-E curves of this system. We suggest that the differences in the Δm-E curves (Fig. 10a) arise because of the heterogeneity of the evaporated gold electrode surface that cause differences in the rate of the forward and reverse redox process.

Adzicet al. studied the UPD of lead at a polycrystalline, evaporated gold electrode, and at (111), (100), and (110) single crystal gold electrodes in 1 M HClO₄ by linear sweep voltammetry, reflect-
Pb(ClO$_4$)$_2$, (c) 0.1 M NaCl containing (111), (110), and (100) faces (shown in Fig. 2, 3, and 4) and different kinds of adsorption sites (a, b, c, d, e) on a gold surface concomitant polycrystalline gold electrode was at least as homogeneous as single-crystal gold electrode involved several adsorption sites. The evaporation spectroscopy, and XPS. They found the microstructure of a single-crystal electrodes on the quartz crystal.

The experimental data shows five reduction and oxidation peaks in chloride medium. We present a model that encompasses five different kinds of adsorption sites (a, b, c, d, e) on a gold surface containing (111), (110), and (100) faces (shown in Fig. 2, 3, and 4) and assign the crystallographic faces as follows. Site a has the (111) orientation, site d has the (100) orientation, and site e has the (110) orientation. Site b corresponds to the boundary between (111) and (110) orientations, and site c corresponds to the boundary between (111) and (100) orientations. The multiple peaks of UPD lead are caused by selective adsorption and deposition on these different gold surface sites. Using this model of the gold surface, we propose a UPD lead deposition mechanism in Fig. 2 for a perchlorate medium with a small portion is adsorbed on site b. As seen in Fig. 6a and 10a, this occurs between about +0.3 V and about −0.10 V. In the potential range −0.10 to −0.3 V, adsorbed Pb(II) on site b is reduced to Pb(0). More dissolved Pb(II) diffuses to the gold surface where it is reduced to UPD Pb(0) on sites a and c, commencing with the second and third cathodic peaks near about −0.24 V. At this juncture, the gold surface is covered by a monolayer of UPD Pb(0). However, our adsorption data and stepwise formation constant data$^{11}$ suggest the next step is

$$\text{Pb}^{2+}(\text{H}_2\text{O})_{4-x}(-\text{Cl}^-)_x + (3 - x)\text{Cl}^- + \text{Cl}^- - \text{Au} \rightarrow \text{PbCl}_4^{2-} - \text{Au} + (4 - x)\, \text{H}_2\text{O}$$

where x is either 1 or 0. It differs from the mechanism given by Eq. 3 and 4 in that the metal species in solution is only partially coordinated to the ligand, and dissolved ligands are required to form an adsorbed species with more coordinated ligands.
Correlation of EQCM data in Cl$^{-}$ and ClO$_{4}^{-}$ media.—Figure 9a-c are $\Delta m$-$Q$ curves for 7.7 $\times$ 10$^{-2}$ M Pb(II) solutions in 0.1 M NaCl + 10$^{-4}$ M HCl or in 0.1 M NaClO$_{4}$ + 10$^{-4}$ M HClO$_{4}$ solutions. Curve 9b was prepared using Pb(CIO$_{4}$)$_{2}$. The other two curves were prepared using Pb(NO$_{3}$)$_{2}$. They were obtained simultaneously with the I-E curves shown in Fig. 6a-c. We assume that all the EQCM electrodes we used had some roughness. Then the total charge consumed to form one monolayer of Pb UPD in 0.1 M NaCl + 10$^{-4}$ M HCl medium should be equal to the total charge, 176 $\mu$C, required in 0.1 M NaClO$_{4}$ + 10$^{-4}$ M HClO$_{4}$ medium. Based on this assumption, the mass axes in Fig. 9, curves a, b, and c, were translated to coincide at a total charge of 176 $\mu$C.

Two EQCM experiments in chloride medium yield the same conclusion, i.e., the adsorption process at +0.3 V is

$$\text{Pb}^{2+}((\text{H}_2\text{O})_4)_2(\text{Cl})_4 + (3 - x)\text{Cl}^{-} + \text{Cl}^{-} - \text{Au} \rightarrow \text{PbCl}_2^{2-} - \text{Au} + (4-x)\text{H}_2\text{O} ; x = 1 \text{ or } 0$$  \[7\]

These two experiments are the Pb(II) injection experiments at +0.3 V, and the one shown in Fig. 9 gives total mass of the adsorbate at Q = 0.

As shown in Fig. 9, the slope CD in chloride medium is the same as the cathodic slopes (slope A’B’ and slope B’C’) in perchlorate medium. Consequently, the same adsorption/deposition processes also occur in chloride medium, namely

$$\text{Pb(II)$_{\text{soln}}$ + 2e}$ \rightarrow \text{Pb(0)}$$  \[8\]

along with a very small amount of Pb(II)$_{\text{ads}}$ being adsorbed on site b, the boundary of (111) and (110) sites. However, a mass decrease with an accompanying cathodic charge increase, absent in perchlorate medium, occurred in chloride medium (region DE and EF).

These phenomena show a desorption process accompanying a cathodic charge increase, absent in perchlorate medium. Chloride adsorption starts to decrease near the cathodic current peak G at $E_{\text{g,c}}$ = −0.14 V (Fig. 6a and b). Dissolved Pb(II) diffuses to the gold electrode and is reduced to Pb(0) at site c and small amounts of Pb(II) adsorb at site c. The m/Q slope for this EQCM process (slope CD) is same as that in perchlorate electrolyte (slope AB’ and B’E’). When nitrate is absent, site d is not occupied; dissolved Pb(II) also reduced at site d in this potential region.

When the potential is scanned from −0.25 to −0.42 V, the mass starts to decrease near cathodic current peak H at $E_{\text{h,c}}$ = −0.3 V. This is where the UPD process nears completion. We rationalized this decrease (see Results and Discussion subsection on Correlation of EQCM data) by assuming that during the UPD process, some adsorbed PbCl$_2^{2-}$$_{\text{ads}}$ on site a is reduced to Pb(0) with ejection of 4Cl$^{-}$. Then the remaining adsorbed PbCl$_2^{2-}$$_{\text{ads}}$ is ejected simultaneously from the Au surface. In this potential range, adsorbed nitrate is partially reduced to adsorbed nitrite. To simplify the diagrams, Fig. 3 and 4 show the adsorbed nitrite, but not the coadsorbed nitrate.

The difference in mechanisms shown in Fig. 3 and 4 is that adsorbed nitrate occupies site d in Fig. 4. In Fig. 3, site d is shown to be occupied by UPD Pb(0) while potential changes from +0.13 to −0.25 V. The nitrate effect is discussed further in the next section.

Anodic oxidation mechanisms in sodium perchlorate electrolyte.—The anodic stripping of lead in perchlorate medium produces a single slope in the $\Delta m$-$Q$ curve (Fig. 9a). The I-E curve (Fig. 6a) for this system shows that in the potential region between −0.42 and −0.30 V, only double layer processes occur. Lead stripping starts at −0.30 V. The corresponding $\Delta m$-$E$ curves (Fig. 10a), exhibit two well-defined steps during the anodic stripping process.

When the potential is scanned from −0.30 to −0.10 V, Pb(0) previously deposited at sites a and c is oxidized to Pb(II) and desorbs into solution as Pb(II)$_{\text{soln}}$. When the potential is scanned from −0.10 to +0.20 V, UPD Pb(0) resident on sites b and e is oxidized to Pb(II)$_{\text{ads}}$.

In the potential range +0.20 to +0.3 V, adsorbed nitrite is oxidized back to adsorbed nitrate, which agrees with the observation seen in Fig. 9a and 10a. That there is anodic charge consumption without any accompanying mass change.

Anodic oxidation mechanism in sodium chloride electrolyte.—The stripping of Pb(0) starts at −0.31 V, as shown in Fig. 6b, c, Fig. 9b, c and Fig. 10b, c and described in Fig. 3 and 4. In the potential region −0.31 to −0.22 V, no significant mass change accompanies the consumption of anodic charge. We rationalize this as the oxidation of UPD Pb(0) at sites a and c to Pb(II)$_{\text{ads}}$. Pb(II)$_{\text{ads}}$ is an anionic species and remains electrostatically adsorbed because the rational potential is positive in this potential region. When the potential changes, from −0.22 to −0.09 V, Pb(0) at site d and/or e is oxidized to Pb(II)$_{\text{ads}}$ with adsorption of dissolved chloride to form PbCl$_2^{2-}$$_{\text{ads}}$ adsorbs on sites a and c. This manifests itself as a mass increase. In the potential range of −0.09 to +0.18 V, the rational potential becomes more positive, and a competition between electrostatic adsorption of chloride to form PbCl$_2^{2-}$$_{\text{ads}}$ and desorption of adsorbed Pb(II) comes into play. Chloride adsorption
may be favored, and some Pb(II) is ejected from the electrode surface and some PbCl$_2^{2-}$ adsorbate remains on the electrode surface. The net mass change is negative because of steric reasons since, e.g., four adsorbed chloride ions would occupy more electrode surface area than one anionic lead complex, but would weigh less. This mass effect is shown in Fig. 10b and c. When the potential is changed from +0.18 to +0.3 V, additional PbCl$_2^{2-}$ adsorb on site b desorbs and adsorbed nitrate is oxidized to nitrate. At +0.3 V, only PbCl$_2^{2-}$ remains adsorbed on site a.

A difference of mass response between −0.42 and −0.19 V is observed in Fig. 10b [0.1 M NaCl + 10$^{-4}$ M HCl containing 7.7 × 10$^{-3}$ M Pb(ClO$_4$)$_2$] and Fig. 10c [0.1 M NaCl + 10$^{-4}$ M HCl containing 7.7 × 10$^{-3}$ M Pb(NO$_3$)$_2$]. In Fig. 10c, no significant mass change occurs between −0.42 to −0.19 V. However, in Fig. 10b, a slight mass increase was followed by a decrease in this potential region. This difference in $\Delta m$-$E$ response between −0.42 and −0.19 V is caused by specific adsorption of NO$_3^-$, as has been shown in Part I.$^{12}$ Also, the $I$-$E$ curves (Fig. 6c) show that the cathodic peaks are more negative than those of Fig. 6b. This is the direction of Pb(0) and its stripping at a polycrystalline gold electrode are consistent with electrostatic adsorption processes expected to occur at Pb(II).

### Conclusion

The adsorption/desorption phenomena observed during the UPD of Pb(0) and its stripping at a polycrystalline gold electrode are consistent with electrostatic adsorption processes expected to occur at positive rational potentials. EQCM experiments in 0.1 M NaCl + 10$^{-4}$ M HCl + 7.7 × 10$^{-3}$ M Pb(II) (as the perchlorate or nitrate) show that faradaic charge passage is due to the formation of UPD Pb(0) or its stripping. Electrode mass changes are also caused by adsorption/desorption of PbCl$_2^{2-}$, Cl$^-$, and/or NO$_3^-$. EQCM data reported here and XPS data reported in Part I$^{12}$ identified the potential dependence of the adsorbed species, their stoichiometry and their surface concentrations. A species with the stoichiometry of PbCl$_2^{2-}$ is adsorbed just before the potential where it reduced to UPD Pb(0). In addition, the adsorbed chloride coverage changes with electrode potential. The specific features of the $I$-$E$ and $\Delta m$-$E$ responses are interpreted assuming that adsorption and UPD deposition occurs at different potentials on the three predominant gold faces present on the polycrystalline gold electrode surface.

EQCM and XPS studies suggest the reduction of adsorbed nitrate ion to adsorbed nitride ion occurs and is catalyzed by Pb UPD formation.$^{23}$

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