Formation of Pb(III) Intermediates in the Electrochemically Controlled Pb(II)/PbO₂ System

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Supporting Information

ABSTRACT: The formation of lead dioxide PbO₂, an important corrosion product in drinking water distribution systems with lead-bearing plumbing materials, has been hypothesized to involve Pb(III) intermediates, but their nature and formation mechanisms remain unexplored. This study employed the electrochemical (EC) method of rotating ring disk electrode (RRDE) and quantum chemical (QC) simulations to examine the generation of intermediates produced during the oxidation of Pb(II) to PbO₂. RRDE data demonstrate that PbO₂ deposition and reduction involves at least two intermediates. One of them is a soluble Pb(III) species that undergoes further transformations to yield immobilized PbO₂ nanoparticles. The formation of this intermediate in EC system is mediated by hydroxyl radicals (OH·), as was evidenced by the suppression of intermediates formation in the presence of the OH· scavenger para-chlorobenzoic acid. QC simulations confirmed that the oxidation of Pb(II) by OH· proceeds via Pb(III) species. These results show that Pb(III) intermediates play an important role in the reactions determining transitions between Pb(II) and Pb(IV) species and could impact lead release in drinking water.

INTRODUCTION

Lead dioxide PbO₂ typically consisting of coalesced nanoparticles is commonly found on lead-containing plumbing materials exposed to drinking water containing chlorine.¹⁻³ Both scrutinyite α-PbO₂ and plattnerite β-PbO₂ form via the oxidation by chlorine of Pb(II) solids including hydrocerussite Pb₃(CO₃)₂(OH)₂, cerussite PbCO₃, and massicot PbO¹⁻⁴⁻⁶ or via the oxidation of Pb(II) solutes.⁶ Because PbO₂ has a very low solubility, its presence is deemed to be beneficial for lead release control. While free chlorine is still widely used for disinfection, many utilities have replaced chlorine with chloramines to reduce disinfection byproduct levels.⁷ However, the switch of disinfectant has been associated with the destabilization of pre-existing PbO₂ and elevated lead in drinking water.⁸⁻⁹ PbO₂ destabilization in the absence of chlorine proceeds via the reduction of PbO₂ to more soluble Pb(II) by natural organic matter,¹⁰⁻¹¹ products of chloramines decay,¹²⁻¹³ and water per se,¹² as well as via colloidal mobilization of PbO₂ particles.¹⁴⁻¹⁵

Because of the complexity of Pb(II)/PbO₂ transformations and their implications to drinking water quality, it is important to understand mechanisms of reactions controlling the oxidation of Pb(II) to PbO₂ and the reduction of the latter. Prior investigations of PbO₂ formation have focused on the identification of batch oxidation products of Pb(II) precursors¹,⁶ or the analysis of structural composition of corrosion scales harvested from distribution systems.⁶⁻⁸ These studies provided valuable information on maintaining the stability of PbO₂ but did not necessarily address the microscopic nature of Pb(II) to Pb(IV) transformations. Our prior studies showed that the oxidation by chlorine of typical Pb(II) solids such as hydrocerussite and cerussite is an autocatalytic reaction catalyzed by Pb(III) intermediates of largely unknown nature and/or nanosize nuclei of PbO₂.⁴⁻⁵

Pb(III) intermediates have only been observed in oxidations with γ-radiolysis, where Pb(II) hydroxo complex Pb(OH)₃⁻ reacted with radiolytically generated hydroxyl radicals (OH·) to produce short-lived Pb(III) species with a hypothetical stoichiometry of Pb(OH)₄⁻ at pH higher than 11.¹⁶ In addition, the presence of Pb(III) intermediates was only hypothesized during the deposition of crystalline PbO₂ in acidic media for battery applications.¹⁷⁻⁻²⁰ However, these studies were carried out in chemical conditions too different from

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drinking water and did not examine the redox properties or molecular structures of Pb(III) intermediates.

Recent studies of the Pb(II)/PbO2 redox system in conditions relevant to drinking water processes indicated a role of Pb(III) intermediates in the formation of surface phases of PbO2. For instance, the reduction of PbO2 to Pb(II) by bromide in acidic solution was hypothesized to proceed via two one-electron transfer steps with the formation of Pb(III) surface intermediates.24 Examination of the oxidation of Pb(II) solids by chlorine also suggested the formation of transient species prior to the generation of PbO2 phase.

To systematically study the formation and redox properties of Pb(III) intermediates in the Pb(II)/PbO2 system, an electrochemical (EC) technique of rotating ring disk electrode (RRDE) was applied to examine directly the generation of such intermediates during the EC formation and reduction of PbO2. Quantum chemical (QC) simulations were performed to gain insight into the structures and ensuing transformations of Pb(III) species generated in these reactions.

**MATERIALS AND METHODS**

**Electrochemical System.** EC experiments were performed using a 125 mL three-electrode cell with a gold RRDE working electrode (Supporting Information Figure S1) affixed to a Pine AFMSRX rotator, a platinum counter electrode, and a Ag/AgCl reference electrode. The principles of intermediates detection is presented in the Support Information. The disk and ring electrodes were controlled by a Pine AFCBP1 bipotentiostat (Pine Instrument Co., Lawrence, KS). The outer diameters of the disk and ring electrodes were 4.57 mm and 5.38 mm, respectively. The ring−disk gap was 0.18 mm. For this electrode geometry and the electrolyte flow dynamics controlled by it, the highest theoretically predicted efficiency of collecting disk-electrode-generated mobile intermediates on the ring electrode is 28%.23 The counter electrode was separated from the working electrode by a glass frit. EC potentials were measured and quoted vs the Ag/AgCl reference electrode (+0.197 V vs the standard hydrogen electrode, SHE).

**Electrochemical and Morphological Measurements.** All EC measurements were carried out in the presence of 0.1 M NaClO4 background electrolyte at 22 ± 2 °C. Prior to each experiment, the surface of the RRDE was polished with microdiamond paste (particle size 0.25 μm) and rinsed with methanol and 0.01 M H2SO4 for 30 s, respectively, and finally with DI water. The reproducibility of the electrode surface preparation was confirmed by cyclic voltammetric (CV) scans in the background electrolyte. The concentration of Pb(II) in the solution was from 0.0001 to 0.005 M. pH values were fixed between 0.5 and 1.3 V. Features of Electrochemical Oxidation of Pb(II). CV scans obtained from the Pb(II)/RRDE system had prominent features that depended on scan rate, rotation speed, solution pH, and evolution of the electrode surface. In static electrode conditions, the first anodic scan carried with E disk potential from −0.4 to 1.5 V showed only one peak with the maximum at approximately 1.2 V (Figure 1A). This peak is denoted henceforth as Peak 2.

For Pb(II) couple can be calculated based on the following expression:

\[
Pb^{2+} + 2H_2O − 2e^- → PbO_2 + 4H^+ \
E^0 = 1.46 V
\] (1)

Under the conditions shown in Figure 1, the EC potential of reaction 1 is 1.1 V vs the Ag/AgCl electrode (Supporting Information Figure S2). The fact that Peak 2 emerged at potentials higher than this threshold indicated that this peak was associated with the EC oxidation of Pb(II) to PbO2. Sequential EC oxidations following the first cycle were accompanied by the emergence of another peak denoted as Peak 1 (Figure 1A). Because Peak 1 emerged at E disk potentials much lower than those of Peak 2 (0.7 to 0.9 V), it corresponded to a reaction involving the oxidation of Pb(II) to intermediate products.

Repeated experiments carried out at E disk less than 1.1 V did not result in PbO2 formation or the occurrence of Peak 1 (Supporting Information Figure S3). SEM examination confirmed that only EC scans exceeding E disk of 1.1 V were accompanied by the formation of a PbO2 phase which also modified the electrode surface (Figure 2). After the first scan, isolated PbO2 nanoparticles with sizes around 30 nm were deposited on the surface (Figure 2A). As the scans continued,
more PbO₂ was accumulated on the electrode and the deposited PbO₂ nuclei aggregated into larger clusters with sizes of approximately 100 nm (Figure 2B). Morphologically, they were indistinguishable from PbO₂ crystallites formed during the oxidation of cerussite and hydrocerussite by chlorine.¹⁴⁻⁶

Peak 1 gained more intensity after each sequential scan and was more sensitive to the solution pH than Peak 2 (Figure 3A).

Figure 1. Main features of voltammetric scans for static gold disk electrode in 0.003 M Pb(ClO₄)₂ solution, pH 5.0, scan rate 75 mV/s. (A) Effects of sequential scans on the evolution of Peaks 1 and 2; (B) positions of main peaks.

Figure 2. Formation of PbO₂ from Pb(II) on the gold electrode surface during sequential cyclic voltammetric scans between −0.4 and 1.5 V. 0.003 M Pb(ClO₄)₂, pH 4.0, background electrolyte 0.1 M NaClO₄, scan rate 50 mV/s. (A) after 1ˢᵗ scan cycle: incipient formation of PbO₂ nanophase; (B) after 5ᵗʰ scan cycle: formation of large PbO₂ clusters.

The ratio of intensities of Peak 1 to Peak 2 increased prominently as a result of the number of scan cycles and also with the increase of solution pH (Figure 3B). The effect of pH indicates that Pb(II) hydroxo complexes were more reactive than free Pb(II) ions in reactions associated with Peak 1, and adsorbed OH⁻ ions may contribute to that reaction. It was also observed that the intensities of Peaks 1 and 2 increased by 2–3 times in rotating electrode conditions (Supporting Information...
Figure S4), suggesting Pb(II) diffusion from bulk solution to the electrode limited the overall reaction rate.

Three peaks corresponding to the cathodic reduction of PbO₂ on the disk electrode were observed. The maxima of these peaks (denoted as Peaks 3, 4, and 5) were located at approximately 0.9, 0.3, and −0.1 V, respectively (Figure 1B). The intensities of Peaks 3 and 4 were not appreciably sensitive to the number of sequential scan cycles, but the intensity of Peak 5 increased steadily in these conditions (Figure 1A). In rotating electrode conditions, Peaks 3 and 4 totally disappeared while the intensity of Peak 5 underwent a nearly threefold increase (Supporting Information Figure S4). These observations indicated that Peaks 3 and 4 were associated with the reduction of hydrodynamically mobile Pb(IV) species, likely precursors of PbO₂ nanoparticles. In contrast, Peak 5 corresponds to the reduction of PbO₂ particles deposited on the electrode surface. Because the amount of PbO₂ deposited on the disk electrode increased after each voltammetric scan and the convection of Pb(II) to the electrode surface was enhanced by rotation, the intensity of Peak 5 increased accordingly.

EC-Generation of Intermediates during PbO₂ Formation and Reduction. The presence of intermediates formed upon the EC oxidation of Pb(II) was confirmed by the ring electrode data obtained in rotating conditions (Figure 4). At pH 4.0 and a scan rate of 50 mV/s, Background electrolyte 0.1 M NaClO₄, pH 4.0. (A) Disk current; (B) ring current at a fixed ring potential of 1.3 V; (C) ring current at a fixed ring potential of 0.7 V; (D) disk current with 25 μM pCBA.

When the ring electrode potential (denoted as \(E_{\text{ring}}\)) was set at 1.3 V, the ring current was constant during the first anodic cycle except decreasing at \(E_{\text{disk}}\) over 1.2 V (Figure 4B). At \(E_{\text{disk}}\) over 1.2 V, the amount of Pb(II) transferred by convection from the disk to the ring decreased due to the oxidation of Pb(II) at the disk electrode. However, following the initial deposition of PbO₂ nuclei on the disk after the first scan cycle, the ring current increased notably at \(E_{\text{disk}}\) potentials located in the Peak 1 region (Figure 4B). Each subsequent cycle that deposited an additional PbO₂ on the disk was accompanied by additional increases of the ring current. This indicated that a hydrodynamically mobile intermediate (denoted henceforth as \(I_{\text{PbIII}}\)) was formed during the oxidation of Pb(II) on the disk electrode and further oxidized on the ring electrode.

Examination of ring currents observed in the \(E_{\text{disk}}\) range close to Peak 2 (from 1.0 to 1.4 V) showed that another EC-active species was generated only after the first anodic scan. In contrast with intermediate \(I_{\text{PbIII}}\), the latter species underwent reduction at the ring when the \(E_{\text{ring}}\) value was set at 0.7 V (Figure 4C). This intermediate (denoted as \(I_{\text{PbII}}\)) was formed at the disk in Peak 2 region. The reduction of intermediate \(I_{\text{PbII}}\) on the ring was observed in the range of \(E_{\text{ring}}\) from 0.6 to 0.8 V with a maximum at 0.7 V (Supporting Information Figure S5). The reduction of PbO₂ deposited on the disk and manifesting itself as Peak 5 was also accompanied by the generation of an
EC-active intermediate whose oxidation also took place in the range of $E_{\text{red}}$ values 0.6 to 0.8 V (Supporting Information Figure S6). This intermediate was denoted as $I_{p3}$.

Because PbO$_2$ was not formed prior to the first anodic scan, the fact that ring currents occurred and increased only after the first scan cycle suggested that the intermediates originated from a reaction that occurred only in the presence of EC-deposited PbO$_2$ and was catalyzed by it. Prior studies show that anodically polarized PbO$_2$ is characterized by high yield of OH$^+$ radicals.$^{31,32}$ During anodic scans, OH$^+$ radicals can be produced on the disk electrode that is deposited with PbO$_2$ and interact with Pb(II) to yield Pb(III) intermediates.

To examine the hypothesis that OH$^+$ radicals generated on the disk electrode are implicated in the generation of intermediate $I_{p\text{HIII}}$, EC experiments were carried out in the presence of pCBA that reacts readily with OH$^+$ radicals.$^{33,34}$ pCBA does not interfere with the electrode surface or Pb species, and its presence did not cause any appreciable changes of the disk currents in the background CV scans. Therefore, pCBA acted exclusively as a OH$^+$ radical scavenger in the EC system. It was found that the presence of 25 μM pCBA suppressed Pb(II) oxidation currents and resulted in less prominent peaks. For instance, the intensity of Peak 1 after four scan cycles was reduced by 40% (Figure 4D) compared with that in the absence of pCBA (Figure 4A). Additionally, ring currents for Peak 2 were suppressed in the presence of pCBA (Supporting Information Figure S7). These results support the notion that intermediate $I_{p\text{HIII}}$ is formed via the oxidation of Pb(II) ions by OH$^+$ radicals produced at the surface of the EC-deposited PbO$_2$.

Examination of relationships between Peak 1 and Peak 5 currents exhibited a strong linear correlation that passed through the origin of the coordinates (Figure 5A). Because Peak 1 and Peak 5 correspond to the production of mobile intermediate $I_{p\text{HIII}}$ and the reduction of EC-deposited PbO$_2$ nanoparticles, respectively, the concerted behavior of these two peaks suggested that the generation of Pb intermediates is intrinsically associated with the formation of PbO$_2$ from oxidizing Pb(II).

In contrast, correlation between Peak 2 and Peak 5 currents never passed through the origin of the coordinates (Figure 5B). Peak 2 was present in the voltammetric scans irrespective of the presence of PbO$_2$. Because EC reactions in the Peak 2 region were still necessary to initiate the deposition of PbO$_2$, only a small fraction of EC reactions at Peak 2 potentials was associated with further oxidation of intermediate $I_{p\text{HIII}}$ (formed at Peak 1 potentials) to PbO$_2$. The remainder of EC currents in the Peak 2 region is likely to be associated with the formation of the other intermediate $I_{p1}$ that did not contribute to the generation of PbO$_2$ solid.

**Quantum Chemical Simulations of Pb(II) and Pb(III) Reactions.** To gain deep insight into the nature of intermediate $I_{p\text{HIII}}$, QC modeling of Pb(II) and Pb(III) reactions was carried out. It started with the examination of the structure of the Pb(II) aqua-complex. Recent experiments show that it tends to have six water molecules in the inner shell, and they cluster on one side of the central Pb$^{2+}$ ion to form an asymmetric (hemi-directed) structure as opposed to a symmetric (holo-directed) distribution of the inner shell water molecules.$^{35-37}$ Optimization of the geometry of Pb(II) aqua-complex PbH$_2$O$_6$$^{2+}$ showed the presence of a pronouncedly hemi-directed arrangement of water molecules (Supporting Information Figure S8-A) in accord with prior experimental data.$^{37}$ The average Pb–O distance determined for the Pb(H$_2$O)$_6$$^{2+}$ ion is 2.59 Å, which compares well with the experimental observations of 2.54 Å.$^{37}$ Further simulations of Pb(II) hydroxo complexes predicted that the presence of OH$^-$ ions in the inner shell of Pb(II) caused the water molecules to migrate to the second hydration shell where they formed hydrogen bonds with the inner sphere ligands. The resultant stoichiometries of thermodynamically favored Pb(II) hydroxo complexes were determined as Pb(OH)(H$_2$O)$_4$$^0$, Pb(OH)$_2$(H$_2$O)$_2$$^-$, Pb(OH)$_3$$^-$, and Pb(OH)$_4$$^{2-}$ (Figure 6A–D).

Interaction of OH$^+$ radical with Pb(H$_2$O)$_6$$^{2+}$ was simulated by adding an OH$^+$ radical to the Pb(H$_2$O)$_6$$^{2+}$ ion to form a Pb(OH)(H$_2$O)$_5$$^{2+}$ complex with an initial Pb–OH$^+$ separation of about 3 Å. This configuration was optimized to yield the structure shown in Supporting Information Figure S8-B. The entry of OH$^+$ into the inner shell resulted in a negligible effective positive charge on the OH$^+$. This particle interacted with the central Pb ion via a weak ion-dipole electrostatic mechanism that resulted in a small negative enthalpy ($\Delta H^0$) value (reaction 1,Table 1). Attempts to force the OH$^+$ radical to approach the central Pb$^{2+}$ ion to a 2.2 to 2.4 Å distance characteristic for Pb(II) hydroxo complexes (Figure 6A–D) resulted in, after full optimization of this starting geometry, the withdrawal of the introduced OH$^+$ radical back to the initial structure shown in Supporting Information Figure S8-A. The effective positive charge on the central Pb ion (+1.8) did not
change appreciably when going from \( \text{Pb(H}_2\text{O)}_{6}^{2+} \) to \( \text{Pb(OH)(H}_2\text{O)}_{6}^{2+} \), indicating that the addition of an OH radical to \( \text{Pb(H}_2\text{O)}_{6}^{2+} \) has a nonoxidative character.

Simulations of interactions of OH radicals with Pb(II) hydroxo complexes showed a different trend. The Gibbs free energy \( (\Delta G^0) \) corresponding to the entry of an OH radical into the inner shell of these complexes decreases with the number of hydroxo groups, indicating increasing thermodynamic likelihood of these reactions (reactions 2–5, Table 1). This is consistent with the EC data demonstrating a pronouncedly more rapid onset of the generation of Pb(III).
intermediates and their higher yields at increasing pHs (Figure 3).

QC simulations showed that the OH radical entering the inner shell of Pb(II) hydroxo complexes acquires a substantial negative charge and becomes nearly identical to the hydroxo groups initially present in the structure. At the same time, the central Pb atom becomes essentially a radical because the major part of the uncoupled electron’s density is located on it. The Pb–OH distances in Pb(OH)₂(H₂O)_₄⁺, Pb(OH)(H₂O)₅⁺, Pb(OH)₂(H₂O)₆⁺, and Pb(OH)₃(H₂O)₇⁺ formed via the interactions of OH radicals with Pb(II) hydroxo complexes ranging from 2.16 to 2.32 Å (Figure 6E–H), much shorter than that in Pb(OH)(H₂O)₅⁺ (2.69 Å). The effective positive charges on the central Pb atom in these intermediates formed by OH radical (Figure 6E–H) are approximately 0.3 to 0.4 more positive compared to those in initial Pb(II) complexes (Figure 6A–D). This indicates that the entry of an OH radical into the inner shell of the Pb(II) hydroxo complexes is a reaction of oxidative addition, and the central Pb atoms can be formally assigned a +3 oxidation state.

The thermodynamics of reactions of Pb(III) species showed that they are susceptible to further oxidation to yield Pb(IV) complexes that can be considered as precursors of PbO₂. ΔG₀ values corresponding to the oxidation of Pb(OH)₂(H₂O)_₄⁺ and Pb(OH)(H₂O)₅⁺ by OH radicals are −31.4 and −37.5 kcal/mol, respectively (reactions 6 and 7, Table 1). The oxidation of Pb(OH)₄⁺ and Pb(OH)₃(H₂O)₄⁺ are expected to predominate at high pHs have ΔG₀ values of −44.3 and −52.7 kcal/mol, respectively (reactions 8 and 9, Table 1).

QC calculations also demonstrated that, in accord with the data of radiolysis experiments, Pb(III) intermediates can undergo dimerization/disproportionation to yield Pb(II) and Pb(IV) species (reactions 10–15, Table 1). ΔG₀ values corresponding to some of these reactions (reactions 10 and 11, Table 1) are slightly lower than those determined for the oxidation of Pb(III) intermediate by OH radical (reactions 6 and 7, Table 1). Pb(IV) complexes (reactions 10–12 and 14, Table 1) are expected to undergo further transformations to form solid PbO₂ phase.

Synthesis of EC and QC Data on Pb(III) Formation. EC data demonstrate that traces of PbO₂ nanoparticles deposited on the electrode after the first CV cycle initiate and catalyze the EC generation of OH radicals, which by reacting preferentially with Pb(II) hydroxo complexes produce Pb(III) intermediates associated with Peak 1. While concentrations of Pb(II) hydroxo complexes are low at pH less than 5, the possibility that they have a much higher reactivity in EC oxidations was confirmed by QC simulations that determine that these intermediates are likely to be Pb(OH)₃(H₂O)_₄⁺ and Pb(OH)(H₂O)₅⁺ (reactions 2 and 3, Table 1).

These Pb(III) species can be directly EC-oxidized or interact with EC-generated OH radicals to form PbO₂ precursors. These reactions are associated with Peak 2 in the EC system. Their occurrence is also supported by the QC predictions (reactions 6 and 7, Table 1). Alternatively, when the concentration of Pb(III) species at the surface is high enough, they are likely to dimerize and disproportionate to yield Pb(IV) species, for example, Pb(OH)₂(H₂O)₄⁺ and Pb(OH)₃(H₂O)₅⁺ (reactions 10 and 14, Table 1) and undergo further transformations to form PbO₂.

Environmental Implications. The electrochemical technique used in this study allowed for in situ detection of Pb(III) intermediates generated during the EC oxidation of Pb(II).

Quantum chemical simulations examined the microstructure and thermodynamic properties of Pb(III) species in solution chemistry with OH radicals. Despite that reactions in the distribution system involve surfaces of lead oxide particles, simulation data unambiguously characterized the reaction pathways involving Pb(III).

Although redox controls in drinking water distribution systems with lead-containing plumbing materials and residual chlorine may be different from those in the studied EC-controlled system because in the latter case the formation of Pb(III) is driven by EC-generated OH radicals while in water distribution systems Pb(II) oxidation is driven by the HOCI/Cl⁻ couple, the intrinsic aspects of the redox chemistry of the Pb(II)/Pb(IV) couple are fundamentally the same in both cases. Thus, the reported measurements of Pb(III) by means of analytical electrochemistry prove that Pb(III) intermediates and Pb(III) generation mechanisms are likely to play an important role in Pb(II) oxidation processes in drinking water. The reduction and destabilization of PbO₂ also involve transient species.

Prior research in environmental systems reported the catalytic role of PbO₂ in the oxidation by chlorine of Pb(II) hydroxylcarbonates, the occurrence of distinct attack sites on the surfaces of these solids which are indicative of the generation of soluble intermediates, and the hypothesized formation of a Pb(III) surface complex during the reduction of PbO₂ by Br₂, which all agree with this study concerning the formation of Pb intermediates during Pb(II)/Pb(IV) redox transformations. In drinking water distribution systems, the generation of Pb(III) from Pb(II) can be at least partially driven by the formation of Cl⁻ radical from HOCI as a one-electron transfer step, catalyzed by PbO₂ in the corrosion scales. Data from prior studies have suggested that the Cl⁻ radical reacts with water to generate the OH⁺ radical. An estimation based on the reported kinetics data indicates that the steady-state concentration of the OH⁺ radical in these conditions may be on the order of 10⁻¹² M.

Water chemistry can strongly influence the formation of Pb(III) intermediates in a distribution system. Our EC data demonstrate that higher pHs favor the formation of one type of Pb(III) intermediates whose presence eventually leads to the deposition of immobilized PbO₂ nanoparticles, while the formation of the other intermediate that results in mobile Pb(IV) precursors is not very sensitive to pH. Quantum chemical simulations show that this is related to the higher reactivity of Pb(II) hydroxo complexes. However, the concentration of HOCI decreases fast at pH higher than 7 and OCI⁻ is largely unreactive toward Pb(II) species (pK₅HOCI = 7.6). Therefore, there is likely a range of optimal pHs that benefit from the formation of a stable PbO₂ phase in chlorinated water.

Increase of alkalinity in drinking water will increase the concentration of Pb(II) carbonate complexes. Although we did not examine their effects in the EC system, prior research has demonstrated that Pb(II) carbonate complexes are much less reactive with chlorine than Pb(II) hydroxo complexes. Accordingly, the formation of Pb(III) intermediates is expected to be slower in high alkalinity water. Natural organic matter (NOM) in drinking water can form complexes with Pb(II) and possibly Pb(III) species and also scavenge CN⁻ and OH⁺ radicals, thus ultimately affecting the yields of the intermediates. The identities and actual occurrence formed in the presence of NOM will be elucidated in the future.
ASSOCIATED CONTENT

Early figures show the configuration and working principles of the EC experimental system, additional SEM and CV data for EC oxidations of Pb(II) in static and rotating conditions, and selected QC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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