

Detection of Pb(III) Intermediates During the Formation of Nano-phase PbO₂ via Pb(II) Oxidation: An Electrochemical Study

by Haizhou Liu

Lead is one of the most dangerous environmental contaminants but its mobility is dramatically affected by its oxidation state (+2 or +4). Lead dioxide PbO₂ existing as a highly dispersed nano-phase is commonly found in corrosion scales formed in drinking water distribution systems where lead-containing materials are still widely used. Lead dioxide is formed via oxidation by chlorine of Pb(II) solids found in corrosion scales.¹ Oxidation of lead (II) species and, in drinking water conditions, attack by chlorine are possibly associated with the generation of unstable Pb(III) intermediates, which greatly impact all aspects of the formation of PbO₂ nano-particles and release of highly toxic lead.² Despite the practical and fundamental importance of these processes, formation of Pb(III) intermediates, especially in drinking water conditions, has scarcely been explored. This study employs electrochemical (EC) methods to quantify the generation of Pb(III)

intermediates, specifically with the technique of Gold Rotating Ring Disk Electrode (Au/RRDE). It's aimed at establishing an RRDE protocol to detect Pb(III) intermediates and PbO₂ nanophase formation during the EC oxidation of Pb(II) species.

EC experiments were performed using a Pine AFMSRX rotator and a Pine AFCBP1 bipotentiostat potentiostat. A conventional 125 ml EC cell with a separated counter-electrode compartment was employed. Pb(ClO₄)₂ solution was chosen as the Pb(II) specie for EC oxidation, with its concentration ranging from 0.0001 to 0.005 M and pH from 3 to 5. Before each experiment, the electrode was polished with micron-sized diamond paste, rinsed with methanol and 0.01 M H₂SO₄ for 30 seconds, respectively, and cleaned with DI water. Voltammetric measurements were carried out in 0.1 M NaClO₄ background electrolyte. The scan rate varied from 25 to 300 mV/s, and the rotation speed changed from 250 to 1000 rpm. The potential of disk electrode was scanned between -0.4 to 1.5 V for multiple cycles, and the potential of ring electrode was fixed at different values between 0.5 to 1.3 V in different experiments. All potentials are quoted versus the Ag/AgCl reference electrode. The temperature was 25°C.

During the EC oxidation process with rotating ring disk electrode, Pb(II) was oxidized on the surface of the disk electrode to PbO₂ during the anodic scan. It was expected, based on our hypothesis, that if Pb²⁺ oxidation process Pb(III) intermediates, these intermediates generated on the surface of the disk electrode would be detected on the ring electrode.

Figure 1 shows a typical result of cyclic voltammetry. In this case, the disk electrode potential was scanned between -0.4 to 1.5 V for 5 scan cycles, and the ring electrode potential was fixed at 0.7 V. For the first scan cycle, disk current exhibited only one peak at the potential *ca.* 1.2 V, which corresponds to the formation of PbO₂ from Pb(II), but no ring current was detected. This indicated that the Pb(II) oxidation was initially a one-step two-electron transfer process. However, after the first scan cycle, as a small amount of nanophase PbO₂ were formed and deposited on the surface of the disk electrode, the voltammetry changed substantially. An additional disk current peak occurred at 0.85 V, and a reduction peak showed up in the ring current at 1.1 V (Fig. 1). It is hypothesized that the first disk current peak at 0.85 V corresponds to Pb(III) formation. As Pb(III) intermediates

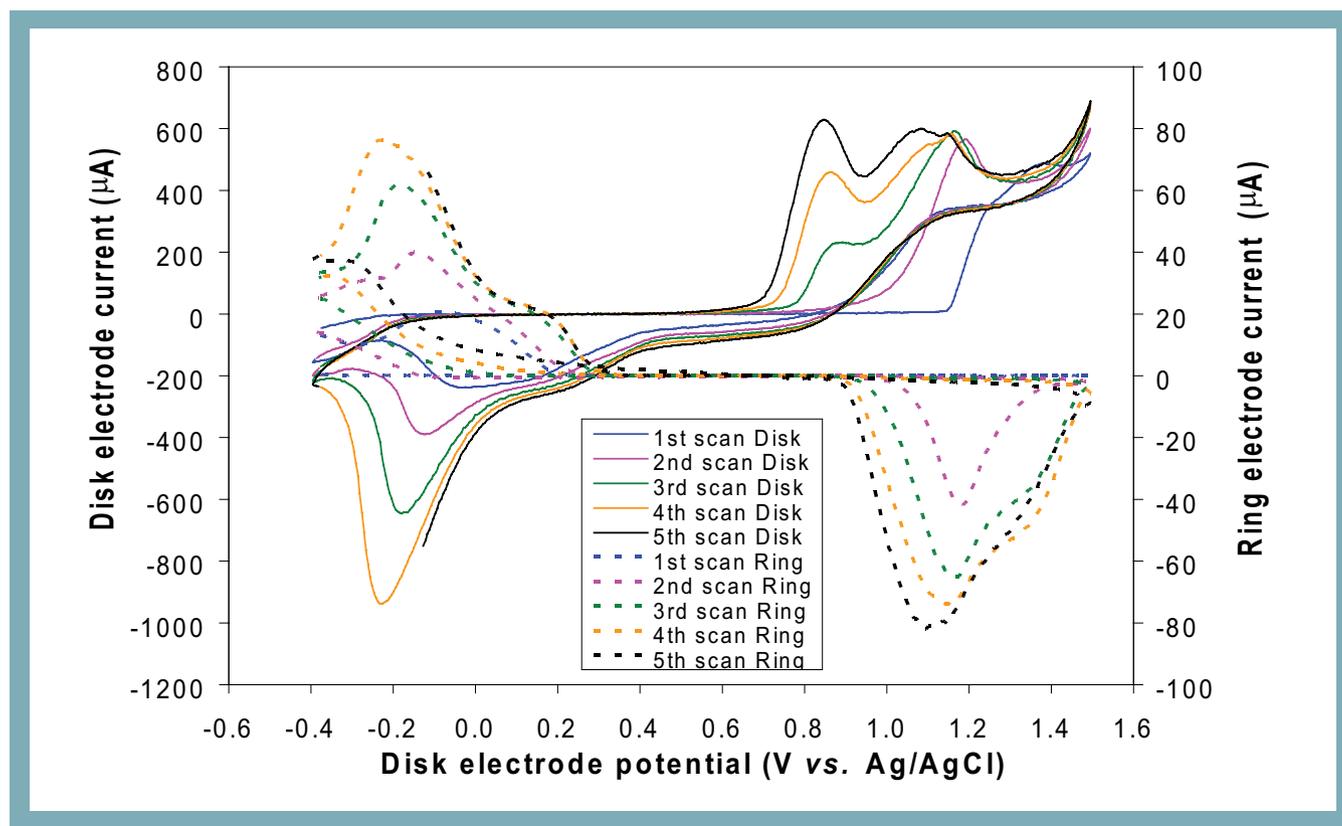


Fig. 1. Impact of scan cycles on cyclic voltammogram for 0.003M Pb(ClO₄)₂. Rotation speed 500 rpm, ring electrode potential 0.7 V, scan rate 50 mV/s, pH 4.0. (Solid lines represent disk currents; dashed lines represent ring currents.)

were formed in the range of potentials, they were detected at 0.7 V at the ring where the reduction of Pb(III) to Pb(II) took place. In addition, the intensity of the peaks increased as the scan cycle increased, which is in accord with the autocatalytic mechanism proposed in our prior study² in that as more PbO₂ were deposited on electrode surface after each scan, it catalyzed the formation of Pb(III).

The nature of Pb(III) intermediates is currently under investigation. Previous studies on PbO₂ deposition in acidic media suggested Pb(III) is formed in the presence of hydroxyl radicals OH· that is adsorbed on electrode surface.^{3,4} In drinking water conditions, OH can be formed via interactions of chlorine and water, although its yield in most reactions is low. In our EC system, if OH· is formed at disk potential >0.8 V, it can oxidize Pb(II) to Pb(III) and subsequently from Pb(III) to PbO₂. To test whether OH· controls the formation of Pb(III) intermediates, similar EC experiments were carried out in the presence of the hydroxyl radical scavenger compound *tert*-butanol. When 3M *tert*-butanol was added, ring and disk currents corresponding to Pb(III) intermediates were suppressed (Fig. 2). This indicates that the formation of Pb(III) is controlled by OH·; the EC production

of this species is catalyzed by nano-phase of PbO₂ deposited during the voltammetric cycling of the electrode.

In summary, this study used EC methods to probe in the formation of Pb(III) intermediates during the oxidation of Pb(II) to PbO₂, a process that has not been examined in the environmental chemistry field. Results show that the EC generation of Pb(III) compounds is mediated by hydroxyl radicals whose yields increase once the electrode surface is modified by nano-nuclei of PbO₂. Detailed experiments are being carried out to further confirm this new finding and determine its implications.

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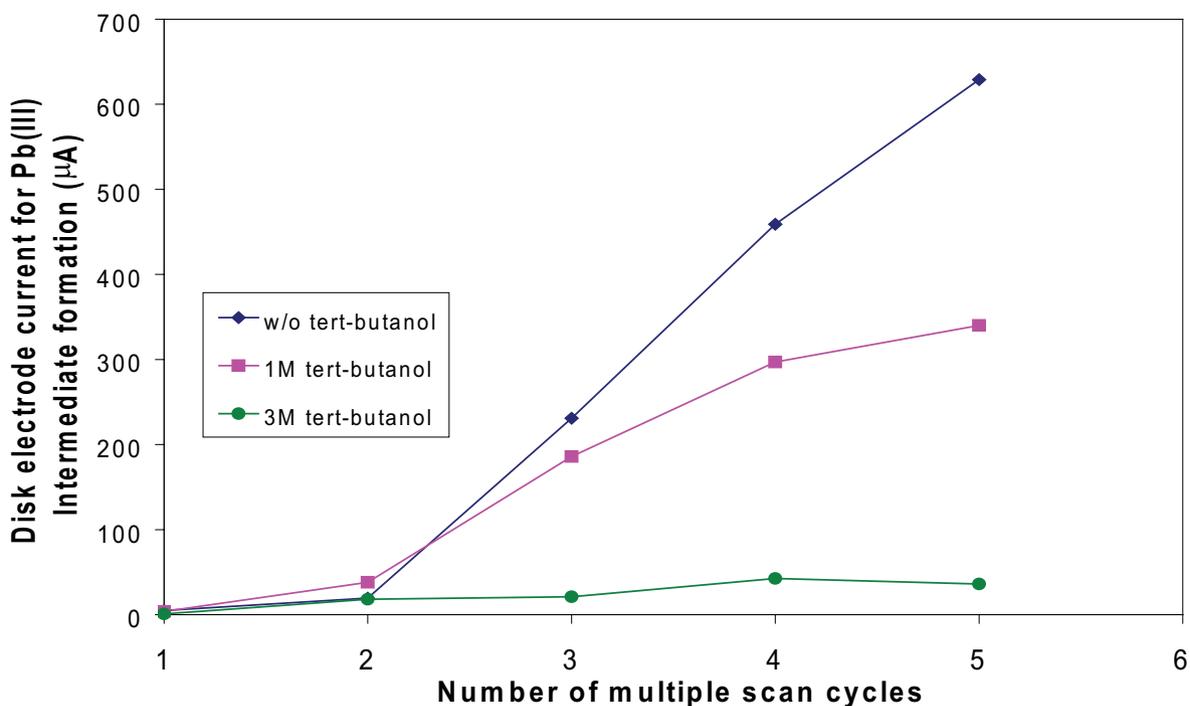


Fig. 2. Changes of the disk current peak intensity for Pb(III) intermediates formation with hydroxyl radical scavenger.