

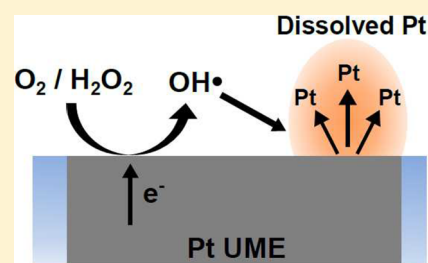
Cathodically Dissolved Platinum Resulting from the O₂ and H₂O₂ Reduction Reactions on Platinum Ultramicroelectrodes

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S Supporting Information

ABSTRACT: The cathodic dissolution of platinum, resulting from the oxygen reduction reaction (ORR) or hydrogen peroxide reduction on platinum, has been investigated. Highly oxidizing hydroxyl radicals (OH[•]) are believed to be the species responsible for the platinum dissolution phenomenon. These radicals are produced from the ORR byproduct, hydrogen peroxide, through a 1 electron reduction pathway (H₂O₂ + e⁻ → OH[•] + OH⁻). Platinum ultramicroelectrodes (UMEs) were polarized sufficiently negative to drive the ORR or H₂O₂ reduction on the platinum surface, mainly using square wave potential pulses but constant applied potential and cyclic voltammetry (CV) were also investigated. The dissolved platinum was detected using a femtomolar level detection technique which involves reducing platinum ions to platinum metal species followed by an electrocatalytic amplification of proton reduction on an inert carbon fiber electrode. This method has allowed the quantification of the amount of platinum metal dissolved into the solution, from which the rate of platinum dissolution could be determined. Additionally, the detection method demonstrates the platinum is dissolved into the solution as an ionic species and does not form metallic nanoparticles.



Recent papers have shown that platinum dissolution can occur at negative potentials when large cathodic currents are flowing.^{1–4} Previously platinum was shown to dissolve at potentials where anodic currents flow and dissolution under these conditions has been widely studied, but cathodic platinum dissolution is still a poorly understood process. Most of the oxidation studies suggest formation of platinum oxide at positive potentials is necessary for platinum dissolution. At sufficiently negative potentials, where cathodic currents flow, the platinum is generally believed to be cathodically protected from forming an oxide layer and subsequently, dissolving. Because of these preconceptions, platinum dissolution at negative potentials where cathodic currents flow has not been considered possible and has not been widely investigated. Understanding this unusual process can have important ramifications in many fields involving platinum cathode electrocatalysis.^{5,6} Additionally, this process may result in Pt loss on very small platinum ultramicroelectrodes (UMEs) in electroanalysis.

Cathodic platinum dissolution in aqueous solutions has been studied previously under both mild¹ conditions (neutral pH electrolyte with 1 V potential pulses) and very harsh² conditions (10 M NaOH with 10 V pulses). There appear to be more than one process for cathodic Pt loss, one of which involves oxygen as a necessary reactant and we deal here with the lower potential process where the ORR occurs. We discuss the high potential process in the conclusion section.

Noël and Mirkin¹ found that small platinum UMEs will become etched in the presence of oxygen from a few potential pulses (driving the ORR) in neutral pH electrolyte solution and found no change when oxygen was not present. However, no attempts were made to quantify the dissolution rate and

determine if the platinum dissolution resulted in an ionic species or as metal nanoparticles coming off of the surface. Hydroxyl radicals formed as a result from the ORR were the species implicated in causing the platinum dissolution but little was done to shed light on the true oxidizing species responsible for the phenomenon. Our goal was to gain further insight into the mechanism that has oxygen as a necessary component in the cathodic dissolution of platinum and demonstrate the existence and quantify the oxidized Pt species in solution.

A representation of the dissolution and detection process used for this study can be seen in Figure 1. First, a platinum electrode is subjected to a cathodic reaction, e.g., by a series of square wave pulses. These pulses bias the electrode sufficiently negative to cause the ORR to occur at the platinum surface, ultimately dissolving some platinum. The solution is then acidified and used to detect the dissolved platinum on a catalytically inert carbon electrode utilizing a recently demonstrated femtomolar PtCl₆²⁻ detection method.^{7,8} This detection method is similar in nature to the rapidly advancing technique of single nanoparticle collision experiments where the collision of a catalytic nanoparticle onto an inert electrode will cause a sudden increase in current due to the amplification of a catalytic reaction.^{9–15} However, instead of a colliding metal nanoparticle, the technique relies on the collision of dissolved Pt ions, which diffuse to the inert electrode and become reduced to Pt⁽⁰⁾ species. When enough platinum atoms have been reduced on the electrode surface, the platinum species

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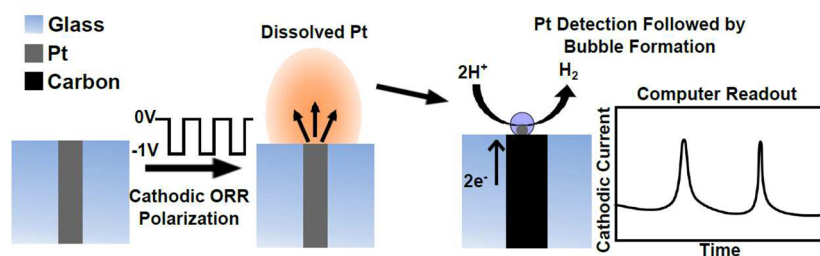


Figure 1. Schematic showing the generalized platinum dissolution from the potential pulsed ORR and the sensitive femtomolar level detection process.

begin to catalyze the reduction of protons in solution, resulting in an increase in the recorded current. The transient current increase is short-lived due to a deactivation process, e.g., nanobubble formation,¹⁶ which shuts off the catalytic reaction resulting in the current “spike” response observed.⁷ The frequency of these “spikes” can be used to determine the concentration of dissolved platinum in the solution from a previously published calibration curve.⁷

RESULTS AND DISCUSSION

The pulsing experiments were performed by first pulsing the Pt UME in an air saturated electrolyte solution driving the ORR followed by acidification of the solution and Pt detection. Typically 100 mM KCl was used but we also tested other electrolytes, including KOH and HCl. The potential pulses were 1 s duration square wave pulses from 0 to -1 V (vs Ag/AgCl), and the number of pulses varied for different trials. The electrochemical experiments were performed in a single compartment electrochemical cell with a carbon counter electrode in a three electrode setup. During the pulse to -1 V, the electrode immediately began to reduce oxygen in solution. During pulses back to 0 V, no anodic faradaic current was observed through the electrode, i.e., there is nothing oxidized. The electrolyte solution was then acidified to a concentration of 1 M H_2SO_4 to perform the platinum collision/detection experiments.

Figure 2 shows some examples of amperometric $i-t$ data curves, following the pulsing experiment, showing the typical platinum detection events where current “spikes” are observed during the trace. The frequency of the “spikes” was used to quantify the amount of platinum dissolved from the electrode. Figure 2A,B shows platinum detection following pulsing in 100 mM KCl or 100 mM KOH, respectively, resulting from 150 pulses applied to a $25\ \mu\text{m}$ Pt UME. The current spikes occur randomly through the duration of the traces indicating the reduction of protons on a platinum species that has formed on the carbon electrode surface, which is biased at a potential where protons will be reduced on platinum but not on the carbon. The current spikes quickly decay back to the baseline, as observed in previously published studies.^{7,8} As a confirmation that the events being detected are in fact due to platinum catalyzing the reduction of protons, an electrode that was detecting the events was then switched from -150 mV to $+100$ mV (vs NHE), shown in Figure 2C. At -150 mV, the reduced platinum species will catalyze the reduction of protons to hydrogen molecules, but when the electrode is switched to $+100$ mV (a potential more positive than the proton reduction potential on platinum) we no longer observe any of the platinum detection events. No spikes were observed for a solution when the cathodic pulsing was not used.

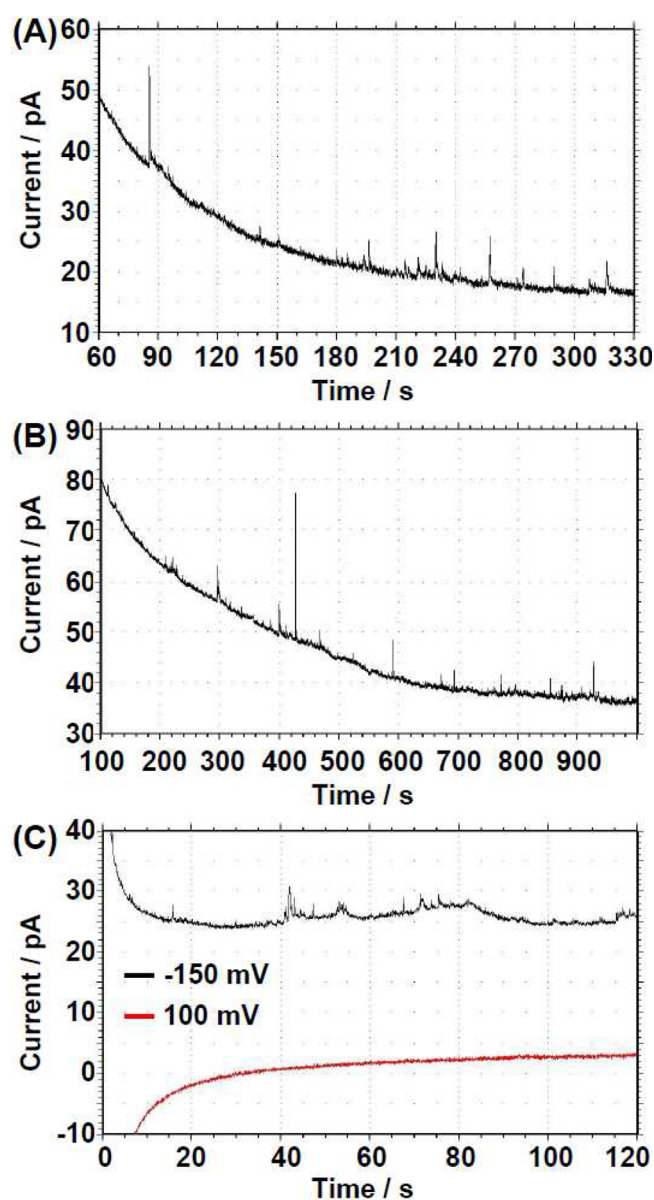


Figure 2. Typical amperometric $i-t$ response for a $10\ \mu\text{m}$ carbon fiber held at -150 mV vs NHE in 1 M H_2SO_4 with dissolved platinum from the pulsing experiment of $25\ \mu\text{m}$ Pt electrodes pulsed 150 times in (A) 100 mM KCl and (B) in 100 mM KOH (both solutions then acidified to 1 M H_2SO_4 concentration for detection). (C) Amperometric $i-t$ curves from a $10\ \mu\text{m}$ carbon fiber in the same conditions as in part A but with two different applied potentials to the carbon fiber during the detection of Pt ($+100$ mV and -150 mV vs NHE).

By quantifying the amount of dissolved platinum that was present after a given number of pulses, the dissolution rate could be determined (see Figure 3). We varied the number of

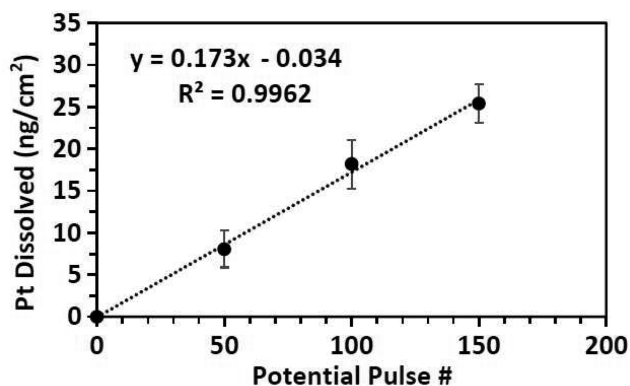


Figure 3. Dissolved platinum (ng/cm^2) versus the number of potential pulses applied to the electrode. Slope of the best fit line is taken as the dissolution rate per pulse. Data collected from $\sim 25 \mu\text{m}$ diameter platinum electrodes in air saturated 100 mM KCl.

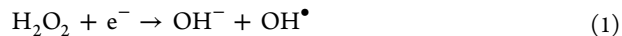
potential pulses applied to $25 \mu\text{m}$ diameter platinum electrodes (50–150, with the same potential pulse described previously) in air saturated 100 mM KCl. The dissolution rates were then calculated in ng/cm^2 and plotted versus the number of potential pulses. From the slope of the best-fit line, the dissolution rate of Pt is approximately $0.173 \text{ ng}/(\text{cm}^2/\text{s})$ in 100 mM KCl. Additionally, in agreement with previous studies,^{1,17} which reported smaller rates in alkaline or acidic solutions, we found that the rate appears to be dependent on the pH of the solution. In sufficiently acidic solutions ($\text{pH} < 2.5$) only slight dissolution was observed. We observed a similar trend where in 100 mM KOH or 10 mM HCl (with 90 mM KCl to keep the same ion concentrations) the platinum dissolution rate slowed, but in 1 mM HCl (with 99 mM KCl) the dissolution was observed to be similar to the neutral pH solution (results listed in the Supporting Information).

According to previous studies there is very little to no observable surface etching (dissolution of platinum¹ or degradation of polymer¹⁷) at these potentials when oxygen is not present in the solution, which agrees with our results from a $25 \mu\text{m}$ Pt electrode pulsed 150 times in deaerated (Ar sparged) 100 mM KCl (Supporting Information). This indicates that the process of the ORR or an ORR byproduct is responsible for the dissolution. In this respect, the dissolution should still happen at a constant potential where the ORR is occurring. The dissolution of platinum was reported as being much slower when the potential is cycled than when pulsing,¹ and so far dissolution at a constant potential has not been reported.

We attempted to quantify the rate of Pt dissolution by applying -1 V bias to a $25 \mu\text{m}$ Pt UME for 1 h in 100 mM KCl (data not shown). We found from detection that the platinum dissolution rate is $0.0065 \text{ ng}/(\text{cm}^2 \text{ s})$ which is ~ 27 times slower than when pulsed. At these constant potentials, the dissolved Pt ions can reduce back to $\text{Pt}^{(0)}$ onto the electrode surface before diffusing away. Additionally, most of the oxygen diffusing to the electrode arrives at the edges, leaving the center of the electrode relatively unused for the ORR at constant potentials and thus not substantially contributing to the overall dissolution. With pulsing, the center of the electrode is actively participating in the ORR for a much larger proportion of the

total time thus allowing an increased rate of dissolution. Basically, the surface is more cathodically protected with a constant applied potential, while with pulsing there are time periods where the diffusing, oxidizing species, probably hydroxyl radical, has a greater chance to oxidize Pt.

It has been proposed that hydroxyl radical (OH^\bullet) is the Pt oxidizing species,^{1,17} since it is a possible intermediate in the ORR as also suggested in other studies.^{18,19} This lends further credence to the hypothesis that hydroxyl radicals are responsible for the cathodic dissolution of platinum. Oxygen can undergo either a $4 e^-$ reduction directly to water or a $2 e^-$ reduction to hydrogen peroxide, which can be further reduced to water.^{20,21} Alternatively, the hydroxyl radical could be produced through the dissociation of the ORR intermediate, hydrogen peroxide, upon reduction. It has been shown in previous studies that platinum will produce a high percentage of hydrogen peroxide during the ORR under certain conditions.^{20,21} Hydroxyl radicals can be formed from hydrogen peroxide through a process known as “reductive-oxidation” where upon reduction, a molecule can dissociate forming a strongly oxidizing radical (i.e., OH^\bullet). This process is employed most in electrogenerated chemiluminescence (ECL) studies where the radical then annihilates a reduced fluorophore, producing light.^{22,23} This has been reported with H_2O_2 where, after a 1 electron reduction, the molecule is said to dissociate forming a hydroxide ion and hydroxyl radical (eq 1).^{22,24}



This reaction can be used to reductively clean an electrode contaminated by an adsorbed layer of organic species. Hapiot¹⁷ showed this with the ORR for etching a polymer film, and we show it is more efficient with H_2O_2 . Here the hydroxyl radical diffuses to the electrode surface modified with a polymer and oxidizes the organic molecules, allowing for site selective etching of the polymer¹⁷ in the vicinity close to the electrode.

Figure 4 demonstrates how the reduction of hydrogen peroxide can generate hydroxyl radicals and effectively clean an electrode that has been fouled by an adsorbed 4-aminothiophenol. The CVs shown in Figure 4A are of a $25 \mu\text{m}$ platinum electrode performing the inner sphere hydrogen evolution reaction where protons are reduced to molecular hydrogen. Before fouling, the reduction of protons readily occurs and quickly reaches the diffusion limited current. However, after fouling the reduction becomes less facile where the reduction wave has shifted to higher overpotentials and does not attain the diffusion limited steady state current as observed on a pristine electrode. Figure 4B shows the recorded amperometric trace during the cleaning procedure in 10 mM H_2O_2 solution. The electrode was biased at -1 V for 60 s causing the reduction of H_2O_2 . The current increased in the beginning of the trace, reaching a plateau after $\sim 15 \text{ s}$ from the beginning. This initial increase in cathodic current is attributed to the hydroxyl radicals cleaning the surface that allows more of the hydrogen peroxide to react. After cleaning, the electrode CV shows the activity for proton reduction has been restored, as seen in Figure 4A. This cleaning experiment again shows that the reduction of H_2O_2 generates hydroxyl radicals which etch away the surface bound molecules cleaning the electrode.

If hydrogen peroxide generates hydroxyl radicals the rate of dissolution from potential pulsing will be accelerated when it is added to the solution. A pulsing experiment was done where a $25 \mu\text{m}$ diameter platinum electrode was pulsed 150 times in 100 mM KCl with the same square wave potential pulse

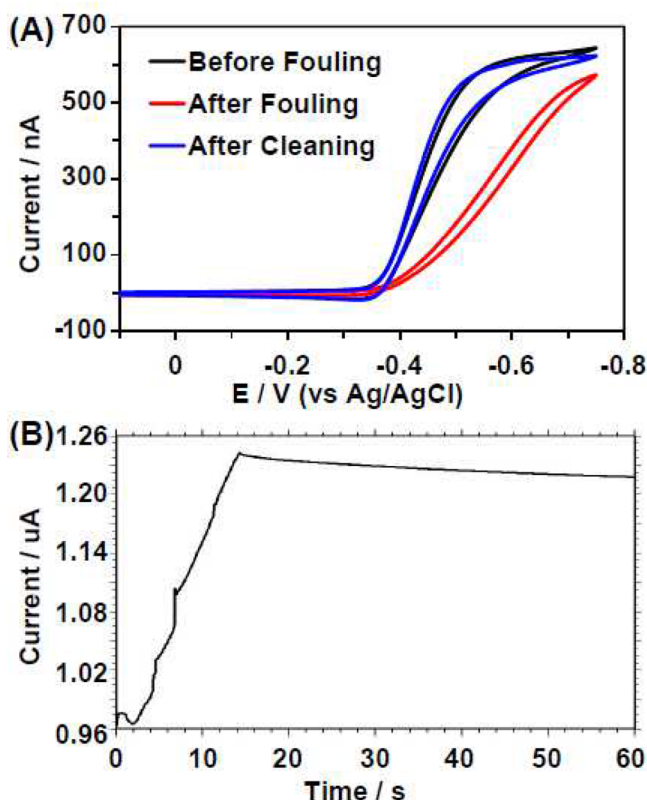


Figure 4. (A) Proton reduction CVs from a 25 μm Pt electrode before adsorption (fouling) of 4-aminothiophenol, after adsorption and after cleaning, acidic solution was 10 mM HCl with 100 mM KCl and the scan rate was 100 mV/s. (B) Amperometric $i-t$ trace during the cleaning procedure of the surface modified 25 μm Pt electrode stepped to -1 V (vs Ag/AgCl) in 10 mM H_2O_2 and 100 mM KCl solution.

described earlier just in the presence of oxygen but with 1 mM H_2O_2 added to the solution. After potential pulsing, the solution was acidified and platinum detection was performed as described previously. The observed rate increased by more than three times than what was observed in just aerated 100 mM KCl (as seen in the [Supporting Information](#)). This increase in dissolution rate when H_2O_2 is added to the solution adds further evidence that the reduction of H_2O_2 generated during the ORR is responsible for the cathodic dissolution of platinum.

Hydrogen peroxide reduction done in the small time scales will effectively clean an electrode with negligible dissolution, but at longer time scales there is a greater probability of dissolution. To highlight and further demonstrate the role hydroxyl radicals play in platinum dissolution, small UMEs (hundreds of nanometer diameter) were used to reduce hydrogen peroxide. Changes in the small electrodes after H_2O_2 reduction can be more easily observed than at larger electrodes through the diffusion limited currents of an outersphere redox molecule. The CVs of two different nanoelectrodes in ferrocene methanol (FcMeOH) are shown in [Figure 5](#). They display the expected sigmoidal shape with a current that plateaus corresponding to the diffusion limited current.²⁵ These currents were used to determine the radius of the electrodes after fabrication according to the disk electrode equation (discussed in the [Supporting Information](#)). The electrode used in [Figure 5A](#) had a calculated radius of ~ 138 nm while the electrode in [Figure 5B](#) was calculated to be ~ 163 nm in radius. Each of these electrodes was used in a H_2O_2

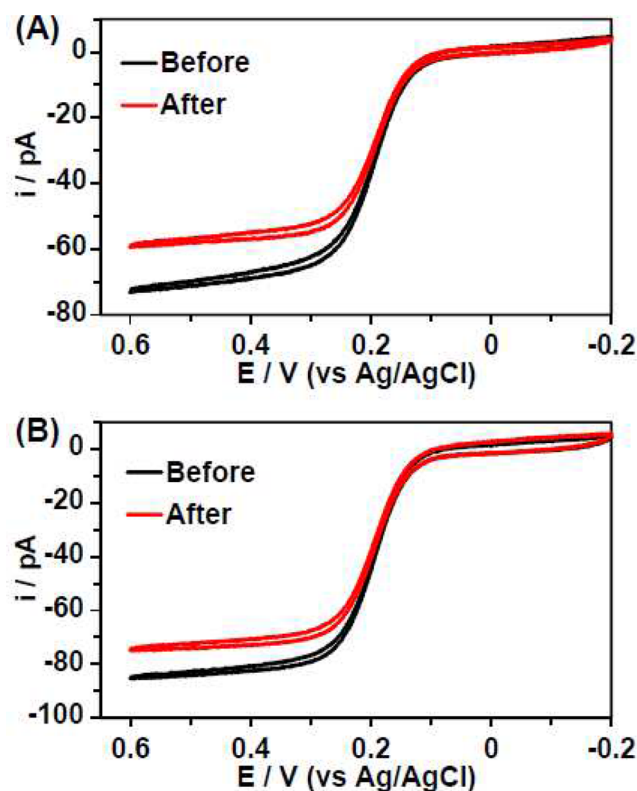


Figure 5. FcMeOH CVs of two nanoelectrodes: (A) a ~ 138 nm radius electrode before and after 20 CVs in 10 mM H_2O_2 and 100 mM KCl and (B) a ~ 163 nm radius electrode before and after 10 min at -0.5 V in 10 mM H_2O_2 and 100 mM KCl. All CVs shown were taken in 2 mM FcMeOH and 100 mM KCl solution at a 50 mV/s scan rate.

reduction experiment and then evaluated to determine if there was any change in the observed currents. The electrode in [5A](#) was cycled a total of 20 times from 0 to -1 V in 10 mM H_2O_2 and 100 mM KCl thus reducing the H_2O_2 . The potential window used will not cause the formation of any oxide on the platinum surface, thus eliminating it as a probable cause of dissolution. After the cycling in H_2O_2 solution the FcMeOH limiting current is reduced by $\sim 18.5\%$ of its initial value, indicating the electrode has recessed by ~ 25 nm after the H_2O_2 reduction CVs. The electrode in [Figure 5B](#) was held at a constant -500 mV potential in 10 mM H_2O_2 and 100 mM KCl for 10 min. This potential is sufficiently negative to reduce the hydrogen peroxide as can be seen from an example CV in the [Supporting Information](#). After this reduction step, the FcMeOH limiting current was observed to decrease by $\sim 12.0\%$ of its initial value indicating a ~ 17.5 nm recession.

In an additional attempt to test the hypothesis that the hydroxyl radical is the species responsible for the platinum dissolution and is not due to an unknown electrochemical reaction, we performed a qualitative experiment where chemically produced hydroxyl radicals could interact with platinum metal. A ~ 25 mm length of 500 μm diameter platinum wire was placed into a solution of 100 mM HCl and 6 mM H_2O_2 and left sitting for 48 h (solution later acidified to 1 M H_2SO_4 for Pt detection). ESR measurements have shown that hydroxyl radicals are formed in solution on platinum metal from H_2O_2 decomposition and detected using a spin trap agent (*S-tert*-butoxycarbonyl-5-methyl-1-pyrroline *N*-oxide).²⁶ [Figure 6](#) is an amperometric $i-t$ curve showing the detection of the dissolved platinum resulting from soaking the wire in the acidic

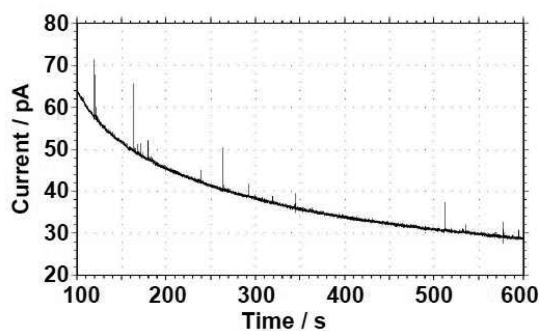


Figure 6. Plot showing the detection of Pt resulting from chemical dissolution in a solution of H_2O_2 . Electrode was a $10\ \mu\text{m}$ carbon fiber biased at $-150\ \text{mV}$ (vs NHE). Solution contained $1\ \text{M}\ \text{H}_2\text{SO}_4$, $10\ \text{mM}\ \text{HCl}$, and $600\ \mu\text{M}\ \text{H}_2\text{O}_2$ after dilution (however, due to the H_2O_2 decomposition on the platinum wire the true H_2O_2 concentration would be lower).

H_2O_2 solution mentioned above. The curve shows clear spikes from the detection of platinum resulting from the attack and dissolution of platinum from hydroxyl radicals. As a control experiment, a wire of equivalent dimensions was placed in a solution of just aerated $100\ \text{mM}\ \text{HCl}$. This control experiment solution gave no response for the detection of dissolved platinum (seen in Figure S-2 of the Supporting Information) and showed that having H_2O_2 present (and thus forming OH^\bullet) does indeed lead to a slow dissolution of the platinum metal indicating hydroxyl radicals are capable of etching platinum metal.

CONCLUSION

We investigated cathodic platinum dissolution resulting from O_2 and H_2O_2 reduction under relatively mild conditions to gain insight into the reaction mechanism and dissolution rate. Our results support that hydroxyl radicals are the oxidizing species for the dissolution of platinum. This mechanism is different from other cathodic platinum dissolution studies^{2–4} where the experimental conditions are much more extreme than conditions tested here. The mechanism we investigated involves the reduction of O_2 (or H_2O_2) as a necessary step in the dissolution process¹ whereas another previously reported mechanism uses high applied potential and results in nanoparticle formation.² The nanoparticle formation is driven by incorporation of electrolyte cations into the platinum metal (effectively forming a negative platinum species).² The high potential method forms metallic nanoparticles and probably does not produce ionic platinum species dissolved in solution, as we found. Other investigations, performed in water and air free, aprotic solvents, found that at very negative potentials ($-1.77\ \text{V}$ vs Ag/AgCl), platinum can corrode through the uptake of electrolyte cations, again forming a negative platinum species, followed by their elimination.^{3,4} There are similarities between the nonaqueous dissolution and the aqueous high potential dissolution which point to a common mechanism, whereas the dissolution of platinum that results from the reduction of O_2 or H_2O_2 can be thought of as wholly different and may have implications in many future studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.analchem.6b04832](https://doi.org/10.1021/acs.analchem.6b04832).

Detailed experimental procedures, chemical list, table listing platinum dissolution rates in different conditions, control experiments, SEM images of electrodes, and additional electrochemical data including example hydroxyl peroxide CVs and sulfuric acid scans (PDF)

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Notes

The authors declare no competing financial interest.

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