Recognizing Single Collisions of $PtCl_6^{2-}$ at Femtomolar Concentrations on Ultramicroelectrodes by Nucleating Electrocatalytic Clusters

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S *Supporting Information*

ABSTRACT: We report the electrodeposition of electrocatalytic clusters of platinum from femtomolar platinate solutions. An inert carbon fiber ultramicroelectrode (UME) was held at a potential where proton reduction was unfavorable on carbon but favorable on platinum in a 1 M sulfuric acid solution. Upon addition of femtomolar amounts of hexachloroplatinic acid, which will also reduce to Pt^0 at the applied potential on the carbon fiber UME, cathodic blips were observed in the amperometric $i-t$ response. These blips correspond to the reduction of protons to molecular hydrogen at the small platinum clusters followed by a rapid deactivation likely due to hydrogen bubble formation. On average, these current spikes occur when five platinum atoms have been formed on the electrode, as determined by a comparative analysis of experimental cathodic blips and calculated hexachloroplatinate molecule collision frequencies.

Electrocatalytic amplification (EA) has been used as a means to study the collision of small nanoparticles on relatively inert ultramicroelectrodes (UMEs).[1−6] In these experiments, the UME is poised at a potential where a reaction of interest, such as proton reduction, is slow, so that when a nanoparticle that can catalyze the reaction collides and sticks to the electrode, a flow of current results. The magnitude of the steady-state current (i_{ss}) response of a single collision depends largely on the concentration of electrocatalytic redox active species, e.g. proton, C_O, and the NP radius, r (eq 1):

$$i_{ss} = 4\pi nrFD_OC_O \ln(2) \qquad (1)$$

where n is the number of electrons transferred in the half reaction, D_O is the diffusion coefficient of the reactant, and F is Faraday's constant. In fact, by assuming proton mass transfer in a 1 M sulfuric acid solution, the current to an electrode of 2 nm radius is expected to be of the order of tens of nanoamperes according to eq 1. The challenge is to use the EA approach on small molecules and ions and the information gained, i.e., response size and shape, to obtain useful chemical properties.

In this report, we describe such an approach for those ions that can be electrodeposited to form an electrocatalytic cluster: here, reducing $PtCl_6^{2-}$ to Pt^0 to catalyze the hydrogen evolution reaction (HER). We show that the method is capable of electrochemically detecting platinum salts at femtomolar concentrations using EA. We also use the experimental frequency of event to estimate the smallest number of platinum atoms required to catalyze proton reduction in the HER.

Figure 1 is a schematic, stepwise representation of the experiment, which consists of the electrodeposition of platinum on a carbon fiber UME in the presence of strong acid. A 10 μm diameter C fiber UME was held at −0.15 V vs NHE in a 1 M sulfuric acid solution containing H_2PtCl_6 at concentrations ranging from 0 to 100 fM. At this potential, the Pt salt can be reduced. For bulk Pt metal, $E° = 0.7$ V vs NHE.[7] At this potential, protons can be reduced on a good electrocatalyst ($E° = 0$ V vs NHE), but not on the C fiber, which requires ca. −0.7 V for H_2 evolution.[8] The electrochemical reactions being driven at the electrode surface are shown in Figure 1. In the first step, the Pt^{IV} ion is reduced to a Pt^0 atom when it diffuses from the bulk solution to the surface of the electrode. Platinum atoms then diffuse on the surface of the carbon electrode, and a cluster forms. In the second step, after a cluster large enough to catalyze and sustain proton reduction forms, faradaic current will begin flowing in the amperometric $i-t$ response due to the reduction of protons on the Pt cluster. In the third step, hydrogen bubble formation occurs due to local H_2 supersaturation around the cluster and then shuts off EA, and a new cluster forms elsewhere on the electrode surface.

The typical experimental response is displayed in Figure 2 when the C fiber UME electrode is poised at −0.15 V vs NHE in a 1 M sulfuric acid solution. Peaks with an intensity of 4 ± 1 pA, an average charge (integration under the $i-t$ response) of 0.45 ± 0.23 pC, and a duration of ca. 500 ms are observed. An estimation of the bubble size can be determined by assuming that all of the charge goes into the formation of a bubble and that the bubble is formed under conditions of standard temperature and pressure. Using these assumptions, passing 0.45 pC of charge corresponds to a bubble of radius 230 nm. Each solution was purged with argon for at least 10 min prior to the amperometric measurements. Control experiments, realized in the absence of platinate salt, did not show cathodic peaks (see Figure S1 in the Supporting Information). When the electrode was held at −0.050 V, where the current for the reduction of protons on platinum is smaller, various current shapes could be observed (see Figure S2 in Supporting Information). The frequency of the cathodic peaks (like those shown in Figure 2A) as measured for various concentrations of Pt salt are plotted in Figure 3A against the concentration of
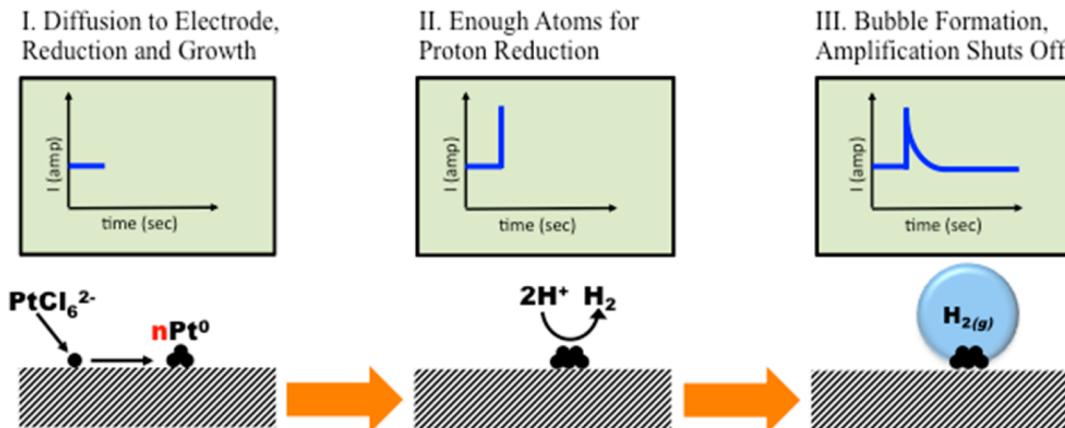
Figure 1. Schematic representation of the experiment and usual amperometric $i-t$ responses that occur when a large enough nucleus of platinum forms, capable of reducing protons to molecular hydrogen.

Figure 3. Frequency of blips versus concentration of hexachloroplatinate for calculated frequency of hexachloroplatinate collisions based on eq 2 (dashed line) and experimental frequency of observed blips (solid line).

Figure 2. (A) Typical amperometric $i-t$ response on a 10 um C fiber UME in 1 M sulfuric acid solution, where the concentration of hexachloroplatinate was 60 fM. The applied potential was −0.15 V vs NHE. (B) Enlargement of some of the data indicating the typical shape of the blips in the presence of hexachloroplatinate.

hexachloroplatinate. The standard deviation for each experimental frequency measurement was less than 10%. The frequency of cathodic peaks varied linearly with the salt concentration, implying diffusion to the electrode surface is the rate-determining step for event observation. The observation of peak-shaped (so-called blips) current responses instead of staircase-shaped current steps indicates that the proton reduction reaction quickly stops, likely due to bubble formation (*vide infra*), which has been previously observed by White and co-workers on nanoelectrodes.[9] Peak-shaped current responses have also been observed for collision with Pt[1] and gold NPs, but not ions, in other electrocatalytic systems.[10]

The diffusional flux of redox active species, $PtCl_6^{2-}$, to the UME, assuming Pt atoms produced remain on the UME surface, can be understood in a stochastic sense by considering

the frequency of collision. The frequency at which molecules of $PtCl_6^{2-}$ collide with the assumed disk UME by diffusion can be calculated by

$$f = 4aD_{PtCl_6^{2-}}C_{PtCl_6^{2-}}N_A \tag{2}$$

where $D_{PtCl_6^{2-}}$ is the diffusion coefficient $PtCl_6^{2-}$, at the viscosity of a 1 M sulfuric acid solution;[11] a is the radius of the inert UME; $C_{PtCl_6^{2-}}$ is the concentration of $PtCl_6^{2-}$; and N_A is Avogadro's number. From the above equation, it is expected that frequency varies linearly with concentration. Figure 3A shows the expected frequency of hexachloroplatinate ion collisions versus concentration (dashed line) overlaid with the frequency of cathodic blips (solid line). The experimental frequency of blips representing proton reduction is about five times lower than the calculated frequency of Pt atom production. If the cathodic blips are indicative of proton reduction on small platinum clusters, then, on average, a total of about five atoms of platinum are present on the electrode surface before an event is observed. Because the frequency at which a blip was observed increased linearly with concentration, the diffusion of platinum atoms on the surface of the working electrode is not the rate-determining step. In fact, an analysis of frequency as a function of time showed no statistically significant deviation over the experimental time frame, as shown in Supporting Information Figure S3.

Table 1. Summary of Data Obtained from Experiments with Platinum

[Pt]/fM	f_{blip} (Hz)	f_{calcd} (Hz)	Pt atoms[a]	t_{avg} (s)	t_{FE} (s)	t_{calcd} (s)	Pt atoms
0	0	0	0	0	0	0	0
20	0.03 ± 0.003	0.17	5 ± 0.5	29.4	33 ± 12	5.9	5.6
40	0.07 ± 0.008	0.34	5 ± 0.4	14.3	15.7 ± 0.95	2.9	5.4
60	0.1 ± 0.009	0.51	5.2 ± 0.4	10	9.9 ± 2.6	2.0	5
100	0.15 ± 0.1	0.86	5.7 ± 0.3	6.7	−	<2	−

[a]Value obtained by taking the ratio of the calculated frequency to the experimental blip frequency.

The time of first event (t_{FE}) is analogous to that given by Boika et al. for the first arrival and collision of insulating spheres on UMEs,[12] and it was used to further test the hypothesis that five atoms of platinum were on the surface of the electrode. In these experiments, the electrode was introduced at $t = 0$, and the time between electrode introduction and the first event was recorded. The average time between Pt deposition events, t_{avg}, and calculated time, t_{calcd}, are simply the inverse of the experimental and theoretical frequencies, respectively. Table 1 gives a summary of the data collected for the experiments with hexachloroplatinate. From these data, the number of platinum atoms on the electrode at the first event was reproducibly between 4 and 6. Table 1 summarizes the results obtained with the platinate experiments and the number of platinum atoms calculated from analyses of frequency of collision and time of first event.

An attempt was made to lower the concentration of acid such that bubble formation would not occur; however, these experiments were not successful. Another effort, using the scanning electrochemical microscope, as shown in Figure 4, was

Figure 4. (A) Schematic representation of the use of the SECM in tip generation−substrate collection mode. The C fiber UME was poised at −0.3 V vs NHE to drive the proton reduction reaction on the Pt nuclei that would form, and the substrate electrode was poised at 0.2 V vs NHE to oxidize the hydrogen gas to protons. (B) Representative data collected curing the SECM experiment with 100 fM $PtCl_6^{2-}$.

also employed to oxidize the hydrogen being evolved at the platinum clusters to decrease the chance that a bubble would nucleate. The scanning electrochemical microscope was used in tip generation−substrate collection mode, as shown in Figure 4. In brief, the C fiber UME was positioned ca. 2 μm from the surface of a larger platinum substrate electrode. The substrate electrode was poised at a potential where molecular hydrogen would be oxidized to protons, causing the immediate environment around the UME to not saturate with hydrogen as quickly and, thus, facilitate bubble dissolution. Even though current blips were also observed in this experiment, the blip height, duration, and charge passed per event were at least an order of magnitude larger than having the substrate electrode turned off. In particular, the blip height was 7 times larger and the average charge passed during the events was 51 times larger. Additional experimental examples of blips with the substrate

turned on are given as Supporting Information Figures S4 and S5.

In conclusion, electrocatalytic amplification has been used as a powerful tool to detect femtomolar concentrations of platinum salts. Furthermore, a detailed analysis of the blip frequency of hexachloroplatinic acid and the considerations of the time of first event at femtomolar concentrations indicates that ca. five atoms of platinum must be on the electrode before proton reduction is detected, which has previously been hard to show in low-concentration platinum experiments.[13,14] We are currently pursuing a similar investigation of other electrocatalytic systems, such as water oxidation with salts of iridium, nickel, and cobalt. One can envisage several analytical applications using electrocatalytic precursors as tags for various colliding analytes of interest.[15,16]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08628.

Experimental methodology and materials (PDF)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Xiao, X. Y.; Bard, A. J. *J. Am. Chem. Soc.* **2007**, *129*, 9610−9612.
(2) Xiao, X. Y.; Fan, F. − R. F.; Bard, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 16669−16677.
(3) Zhou, H.; Fan, F. − R. F.; Bard, A. J. *J. Phys. Chem. Lett.* **2010**, *1*, 2671−2674.
(4) Bard, A. J.; Zhou, H.; Kwon, S. J. *Isr. J. Chem.* **2010**, *50*, 267−276.
(5) Kwon, S. J.; Fan, F. -R. F.; Bard, A. J. *J. Am. Chem. Soc.* **2010**, *132*, 13165−13167.
(6) Bard, A. J.; Boika, A. *Nanoelectrochemistry*; Wiley: New York, 2015; Chapter 8.
(7) Chen, S.; Kucernak, A. *J. Phys. Chem. B* **2003**, *107*, 8392−8402.
(8) Giles, R. D.; Harrison, J. A.; Thirsk, H. R. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *20*, 47−60.
(9) See, for example: Luo, L.; White, H. S. *Langmuir* **2013**, *29*, 11169−11175.

(10) Castaneda, A. D.; Alligrant, T. M.; Loussaert, J. A.; Crooks, R. M. *Langmuir* **2015**, *31*, 876−885.

(11) Rhodes, F. H.; Barbour, C. B. *Ind. Eng. Chem.* **1923**, *15*, 850−852.

(12) Boika, A.; Bard, A. J. *Anal. Chem.* **2015**, *87*, 4341−4346.

(13) Solla-Gullon, J.; Aldaz, A.; Clavilier, J. *Electrochim. Acta* **2013**, *87*, 669−675.

(14) Proch, S.; Wirth, M.; White, H. S.; Anderson, S. L. *J. Am. Chem. Soc.* **2013**, *135*, 3073−3086.

(15) Dick, J. E.; Renault, C.; Bard, A. J. *J. Am. Chem. Soc.* **2015**, *137* (26), 8376−8379.

(16) Dick, J. E.; Boika, A.; Hilterbrand, A. T.; Upton, J. W.; Bard, A. J. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (17), 5303−5308.