

Recognizing Single Collisions of PtCl₆²⁻ at Femtomolar Concentrations on Ultramicroelectrodes by Nucleating Electrocatalytic Clusters

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Flask equilibration:

To obtain accurate femtomolar concentrations from serial dilutions, careful attention was given to flask equilibration. Three 100 mL volumetric flasks were used (one for 20 μ M, 20 nM, and 20 pM solutions), and were equilibrated using the following method: Each flask was filled with about 1 mM metal salt solution and sonicated for 2-8 hours and then let sit at room temperature in a dark environment for 1-3 days.

Chemicals and Reagents:

Water used in each experiment was Milli-Q water (Massachusetts, USA). Phosphate buffer was purchased from Fisher scientific. Ferrocyanide was purchased from Fisher Scientific and used without further purification. Ferrocenedimethanol was purchased from Sigma Aldrich and used without further purification; the main use of this compound was to check the voltammogram of the ultramicroelectrodes. Hexachloroplatinic acid was purchased from Sigma and used without further purification. It is necessary to keep the hexachloroplatinic acid and other platinate salts in a desiccator free from ambient conditions, as it is hygroscopic and will absorb water quickly. High purity sulfuric acid was purchased from Fisher Scientific and used as purchased. Aqua regia was made to clean the working electrode after experiments with platinum by mixing nitric acid and hydrochloric acid in a 1:3 (v/v) mixture. Otherwise, using diamond polish polished the electrode.

Instrumentation:

Electrochemical experiments were performed using a CHI model 920C potentiostat (CH Instruments, Austin, TX). A Ag/AgCl (1M KCl) wire was used (BASi, West

Lafayette, Indiana) as the reference electrode, and a Pt wire was used as the auxiliary electrode. Most potentials are referenced versus the normal hydrogen electrode (NHE), which was converted simply by knowing the relative potentials. A 10 μm carbon fiber was sealed in a glass capillary and polished to expose the working electrode surface, which was slightly recessed. All experiments were carried out using a well-grounded Faraday cage. Each acid solution was purged for 15-20 minutes with argon or nitrogen before the experiments were performed.

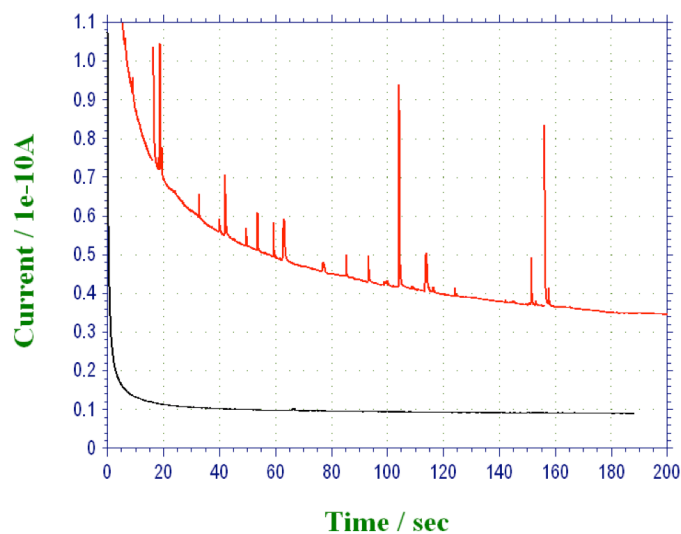


Figure S1. The black curve is without hexachloroplatinic acid and the red curve is with about 100 fM of the PtCl_6^{2-} . The applied potential was -0.15 V vs. NHE.

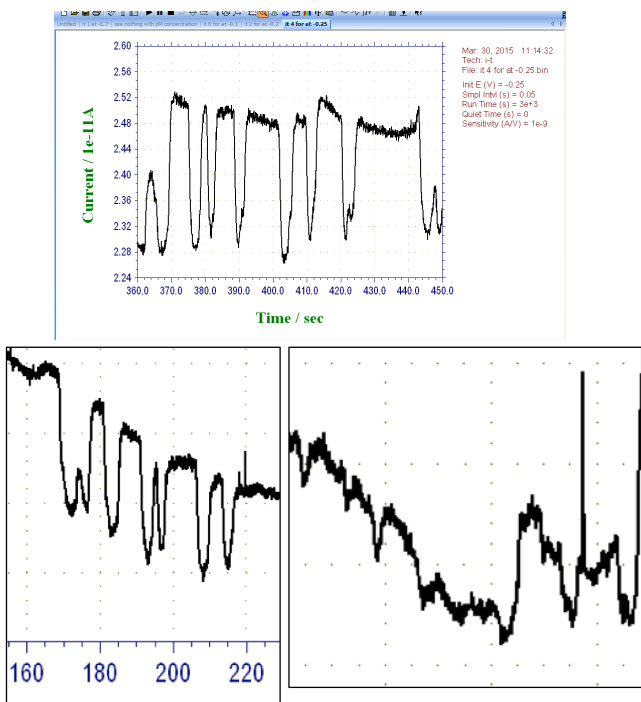


Figure S2. Examples of when the potential is held at -0.05 V vs. NHE in the presence of 60 fM hexachloroplatinic acid.

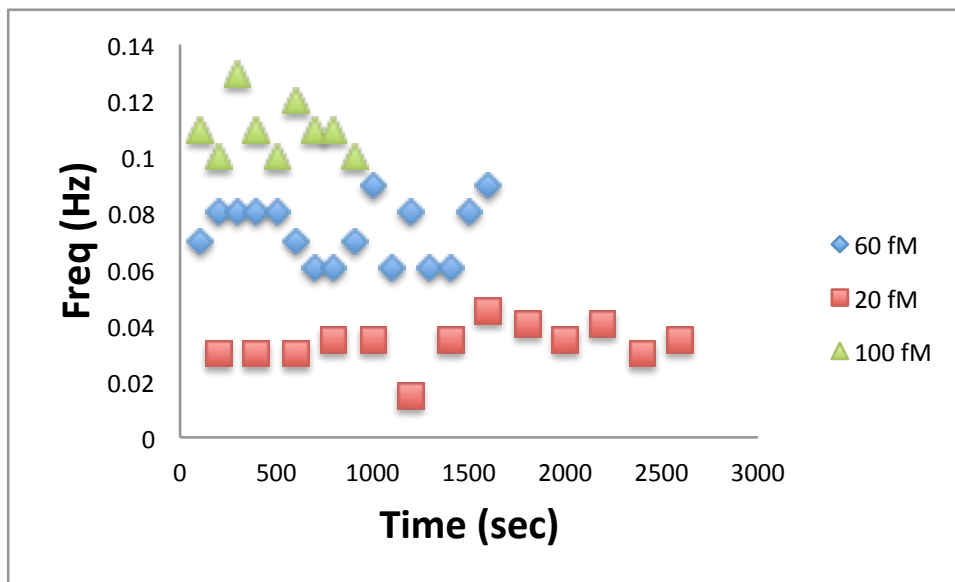


Figure S3. Frequency as a function of time for three different concentrations.

Use of the Scanning Electrochemical Microscope:

In an attempt to provide an environment where a bubble would not form, the scanning electrochemical microscope (SECM) was used. In brief, the C fiber UME was positioned *ca.* 2.5 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, which would cause the immediate environment around the UME to not saturate with hydrogen as quickly and, thus, facilitate bubble dissolution. This substrate is termed the H_2 sink. Even though current blips were also observed in this experiment, the blip height, duration, and charge passed per event were at least two orders of magnitude higher than having the substrate electrode turned off. The C fiber UME approached the substrate electrode by positive feedback in which a 1 mM solution of ferrocene dimethanol was employed. The substrate electrode was poised at a potential where ferrocene was oxidized to ferrocenium, and the C fiber UME (RG = *ca.* 10) was poised at a potential where ferrocenium was reduced back to ferrocene. A schematic of the experiment is given below.

The ferrocene solution was replaced with an acidic solution, which was purged for 15 minutes with argon. Figures S4 and S5 show blip responses when the substrate electrode is turned on. As evidenced by the amperometric *i-t* curves, the current blips are overall larger, which indicates the feedback loop allowing for more protons to be reduced before the deactivation. Overall, the peaks were taller, thicker, and the integral of each peak was larger than when the substrate electrode was turned off. Table S1 gives data tabulated over many experiments contrasting the two scenarios: with and without the substrate electrode turned on. The data are significant because they provide evidence that hydrogen gas is, indeed, being formed on the electrode at a potential where proton reduction is unfavorable on carbon. This gives evidence for the formation of small platinum clusters on the surface of the electrode.

Table S1. Results of blip analysis with and without substrate.

Experiment:	Blip Height (pA)	Charge Passed (pC)
Without SECM	3	0.45±0.23
With SECM	20	23±10

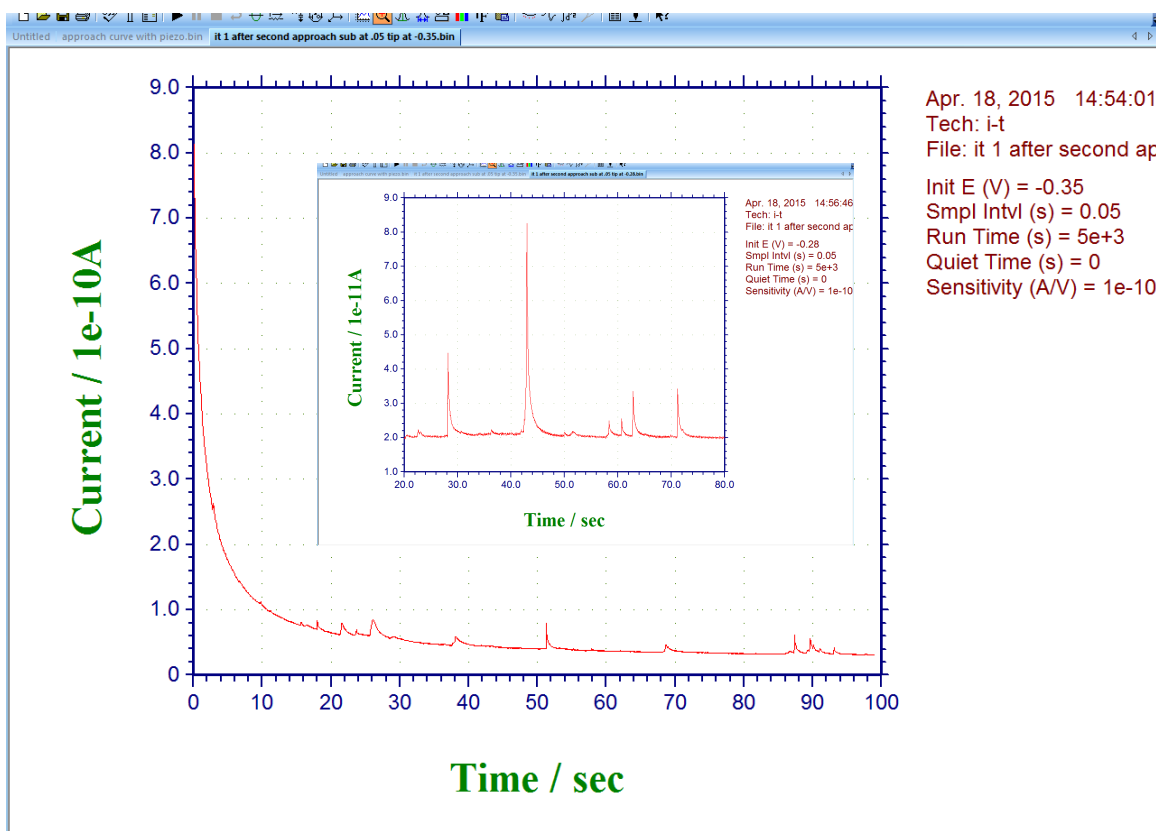


Figure S4. Examples of current blips with the substrate electrode turned on.

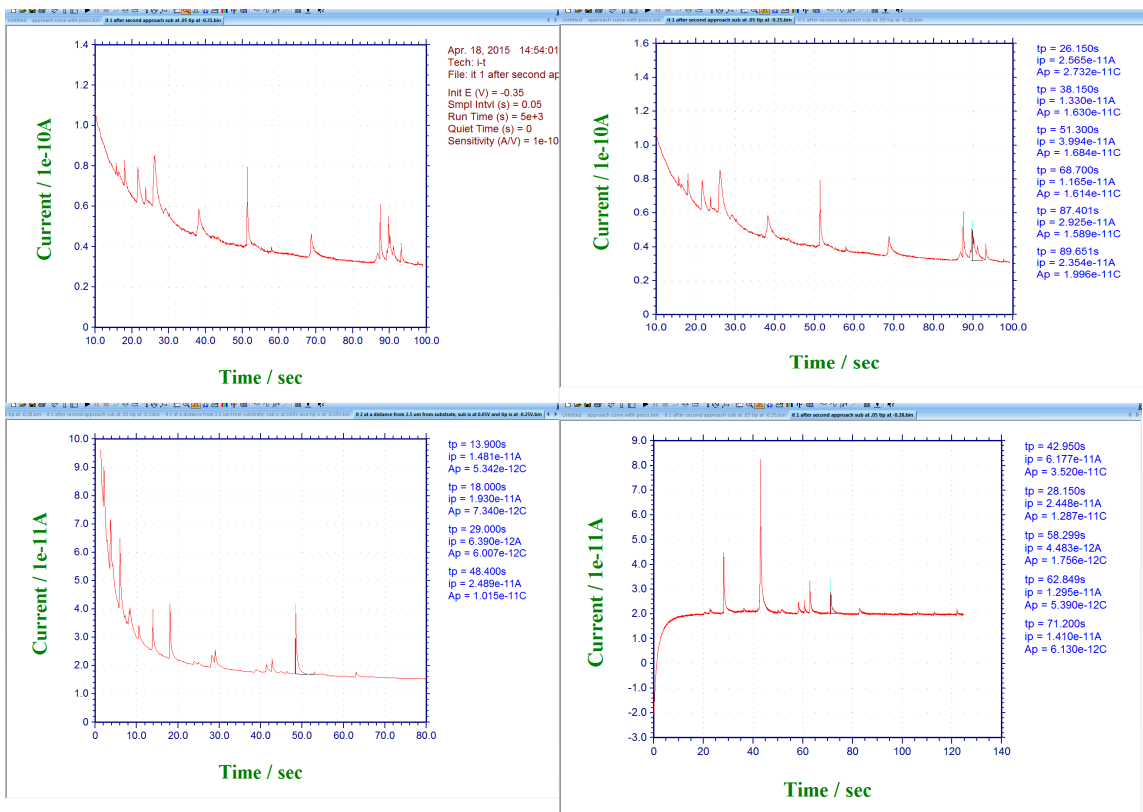


Figure S5. Additional examples of current blips with the substrate electrode turned on.