

Supporting Information: Effect of Large Amplitude AC Modulation on Apparent Reversibility of Electrode Processes

Andrzej S. Baranski* and Aliaksei Boika

Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan,
Canada, S7N 5C9

Email address: andrzej.baranski@usask.ca

* Corresponding author. Tel. (306) 9664701, Fax (306) 9664730

The Supporting Information contains the following material:

Brief description of the simulation program; farther experimental evidence of apparent acceleration of irreversible electrode processes by a superimposed ac modulation (includes: oxide formation/dissolution on Pt in H₂SO₄, redox processes of As(0)/As(III) on gold and reduction of O₂ on gold); evidence of electrochemical etching of Au and Pt by a superimposed ac modulation at 100 kHz; simulated cyclic voltammograms for an irreversible redox process ($k_s = 0.001$ cm/s, $\alpha = 0.65$ and $v = 20$ V/s) with and without a superimposed ac modulation, and analysis of these voltammograms by a convolution method; experimental steady-state voltammograms for the oxidation of 20 mM Fe(CN)₆⁴⁻ in 2 M KCl and 40 mM KCN at a Pt disk microelectrode with a superimposed ac modulation at 10 MHz; and simulated steady-state voltammograms (matching the oxidation of Fe(CN)₆⁴⁻ on Pt) with a superimposed ac modulation at frequencies: 0.1, 1 and 10 MHz.

Numerical Simulation Program. The simulation program created in our laboratory has main components written in Microsoft Visual C++ (and implemented as a dynamic link library) and a user interface written in Visual Basic.

The linear diffusion equation:

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (1)$$

was solved using the explicit finite difference algorithm:^{S-1}

$$f(l,k+1) = f(l,k) + D_M [f(l+1,k) - 2 \cdot f(l,k) + f(l-1,k)] \quad (2)$$

Where: l and k are distance and time indexes, $D_M = \frac{D \cdot \Delta t}{\Delta x^2} \leq 0.5$ (D – diffusion coefficient, Δt – time increment and Δx – distance increment) is the model diffusion coefficient and $f(l, k) = \frac{C(l, k)}{C_{bulk}}$ is the

dimensionless concentration of either the oxidized or the reduced form of the depolarizer.

The boundary condition for the electrode surface was calculated as:

$$f_{ox}(0, k) = \frac{\bar{k}_b + \frac{1}{2} f_{ox}(0, k-1) + D_M [f_{ox}(1, k-1) - f_{ox}(0, k-1)]}{\bar{k}_b + \bar{k}_f + \frac{1}{2}} \quad (3)$$

Where: $f_{ox}(l, k)$ is the dimensionless concentration of the oxidized form of the depolarizer and $\bar{k}_{f or b} = k_{f or b}(E) \frac{\Delta t}{\Delta x}$ is the dimensionless forward or reverse rate constant of the electron transfer process.

This algorithm (based on our derivation) can handle all values of the rate constants (very small and extremely large); therefore, it can be used to model reversible, quasi-reversible and irreversible processes. In addition, simulations can be run for a potential dependent electron transfer coefficient.

The simulations were carried out for planar and hemispherical electrodes. In the case of hemispherical symmetry of diffusion, Fick's equation is written as:

$$\frac{\partial C(r, t)}{\partial t} = D \left[\frac{\partial^2 C(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r, t)}{\partial r} \right] \quad (4)$$

However, this equation can be reduced to eq. (1) by a simple substitution: ^{S-2}

$$\phi(r, t) = rC(r, t) \quad (5)$$

Consequently, the simple algorithm (2) was used in simulations of hemispherical diffusion, but the initial conditions were set according to eq. (5):

$$\phi(l, 0) = r_0 \left(1 + l \frac{\Delta x}{r_0} \right) f(l, 0) \quad (6)$$

Where: r_0 is the electrode radius.

The boundary condition in this case was calculated as:

$$\varphi_{Ox}(0,k) = \frac{\bar{k}_b r_o + \frac{1}{2} \varphi_{Ox}(0,k-1) + D_M [\varphi_{Ox}(1,k-1) - \varphi_{Ox}(0,k-1)]}{\bar{k}_b + \bar{k}_f + \frac{1}{2} + D_M \frac{\Delta x}{r_o}} \quad (7)$$

Finally, the electrode current was calculated as:

$$i(k) = -nFC_b AD_M \frac{\Delta x}{\Delta t} \cdot \left[\frac{\varphi_{Ox}(0,k-1) - \varphi_{Ox}(1,k-1)}{r_o} + \frac{\varphi_{Ox}(0,k) - \varphi_{Ox}(0,k-1)}{2D_M r_o} + \frac{\varphi_{Ox}(0,k) \Delta x}{r_o^2} \right] \quad (8)$$

Where: n is the number of exchanged electrons, F is the Faraday constant and C_b is the bulk concentration of the reactant.

This simulation program was extensively tested by comparing its results with various known analytical and numerical solutions; in all cases the relative errors were lower than 1%.

References:

- S-1. Britz, D.; Digital Simulations in Electrochemistry, 3rd ed.; Springer: Berlin, 2005; Chapter 5.
- S-2. Galus, Z.; Fundamentals of Electrochemical Analysis, 2nd ed.; Ellis Horwood: New York, 1994; Chapter 6.2.

Farther experimental evidence of apparent acceleration of irreversible electrode processes

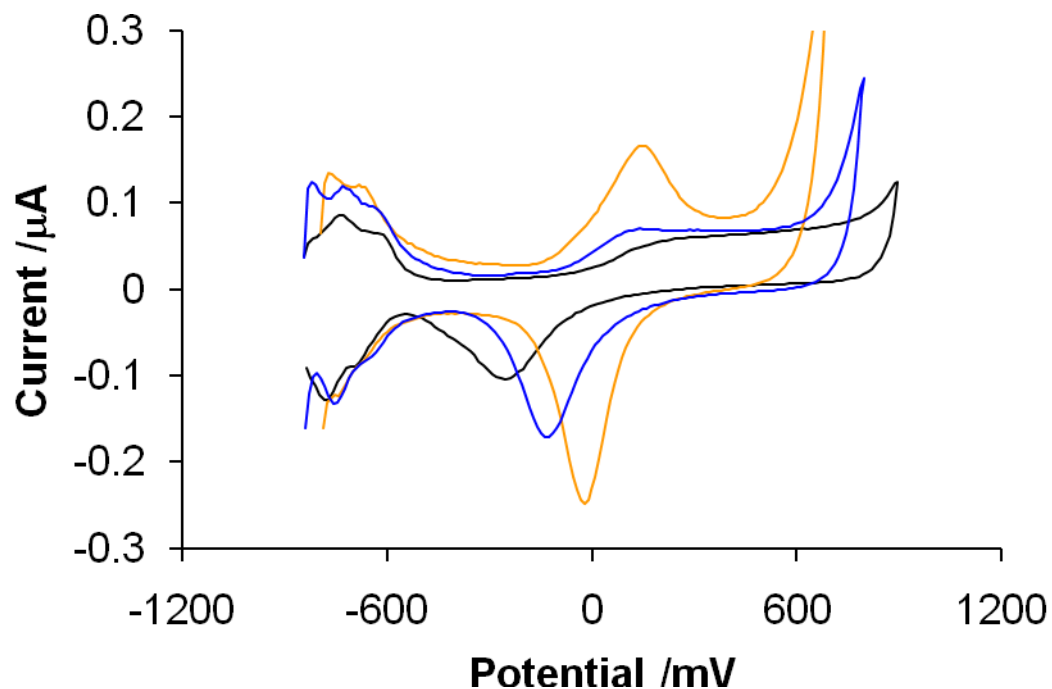


Figure S-1. Cyclic voltammograms obtained with a 25- μm Pt disk microelectrode in 0.3 M H_2SO_4 , without ac modulation (black) and with ac modulation amplitudes 100 mV_{rms} (blue) and 200 mV_{rms} (orange). The frequency of the superimposed ac modulation was 0.1 MHz and the scan rate was 20 V/s.

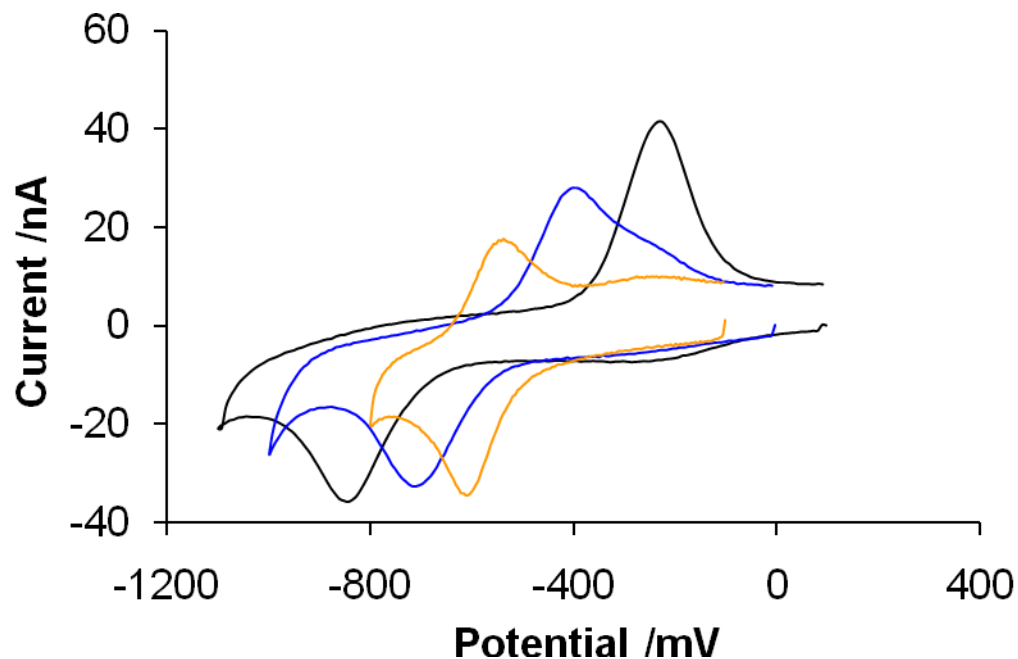


Figure S-2. Cyclic voltammograms obtained with a 25- μm Au disk microelectrode in 0.1 mM NaAsO_2 and 0.01 M H_2SO_4 without ac modulation (black) and with ac modulation amplitudes 100 mV_{rms} (blue) and 200 mV_{rms} (orange). The frequency of the superimposed ac modulation was 0.1 MHz and the scan rate was 20 V/s.

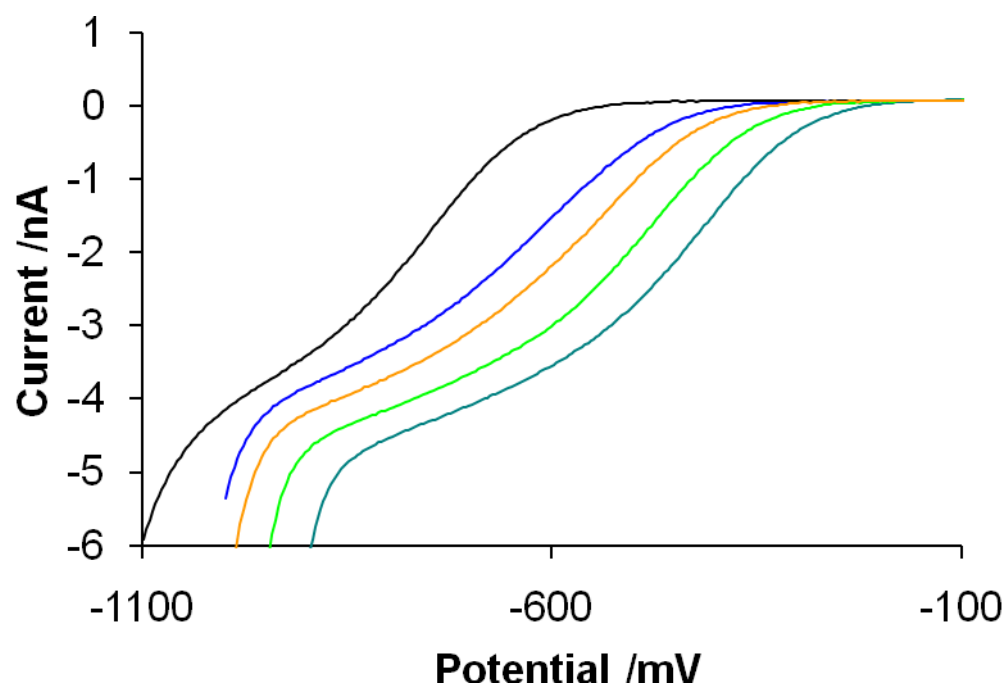


Figure S-3. Reduction of O₂ at a 25- μ m Au disk microelectrode in air-saturated 0.03 M H₂SO₄ without ac modulation (black) and with ac modulation amplitudes 100 mV_{rms} (blue) and 200 mV_{rms} (orange). The frequency of the superimposed ac modulation was 0.1 MHz and the scan rate was 0.02 V/s.

Evidence of electrochemical etching of Au and Pt

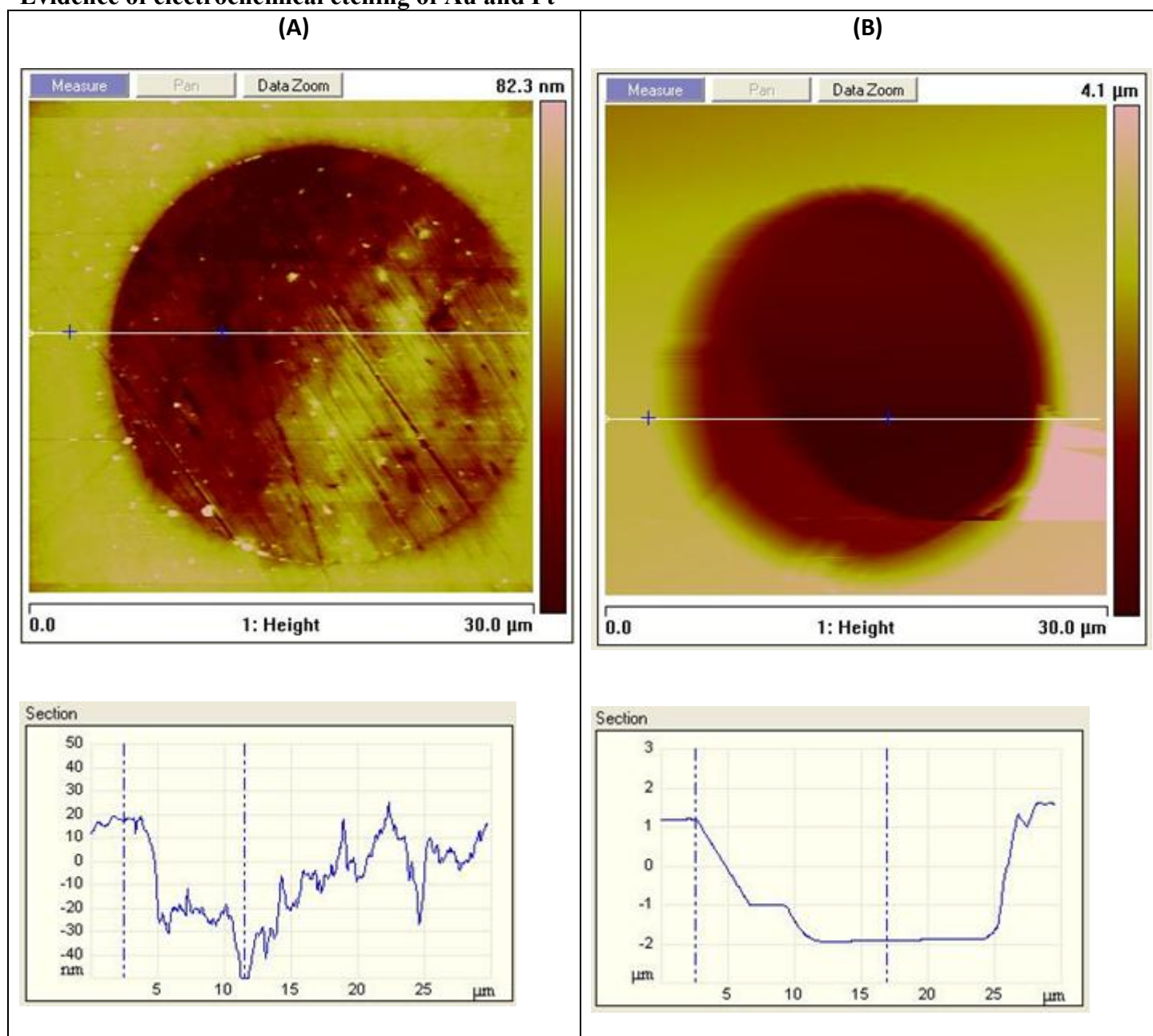


Figure S-4. AFM topography images with corresponding cross sections obtained for a gold microelectrode. (A) – a fresh microelectrode; (B) – a microelectrode after 1 min. of ac modulation (0.3 V_{rms} , 0.1 MHz) in 0.2 M HCl at $E_{\text{dc}} = 1.6$ V vs. SCE.

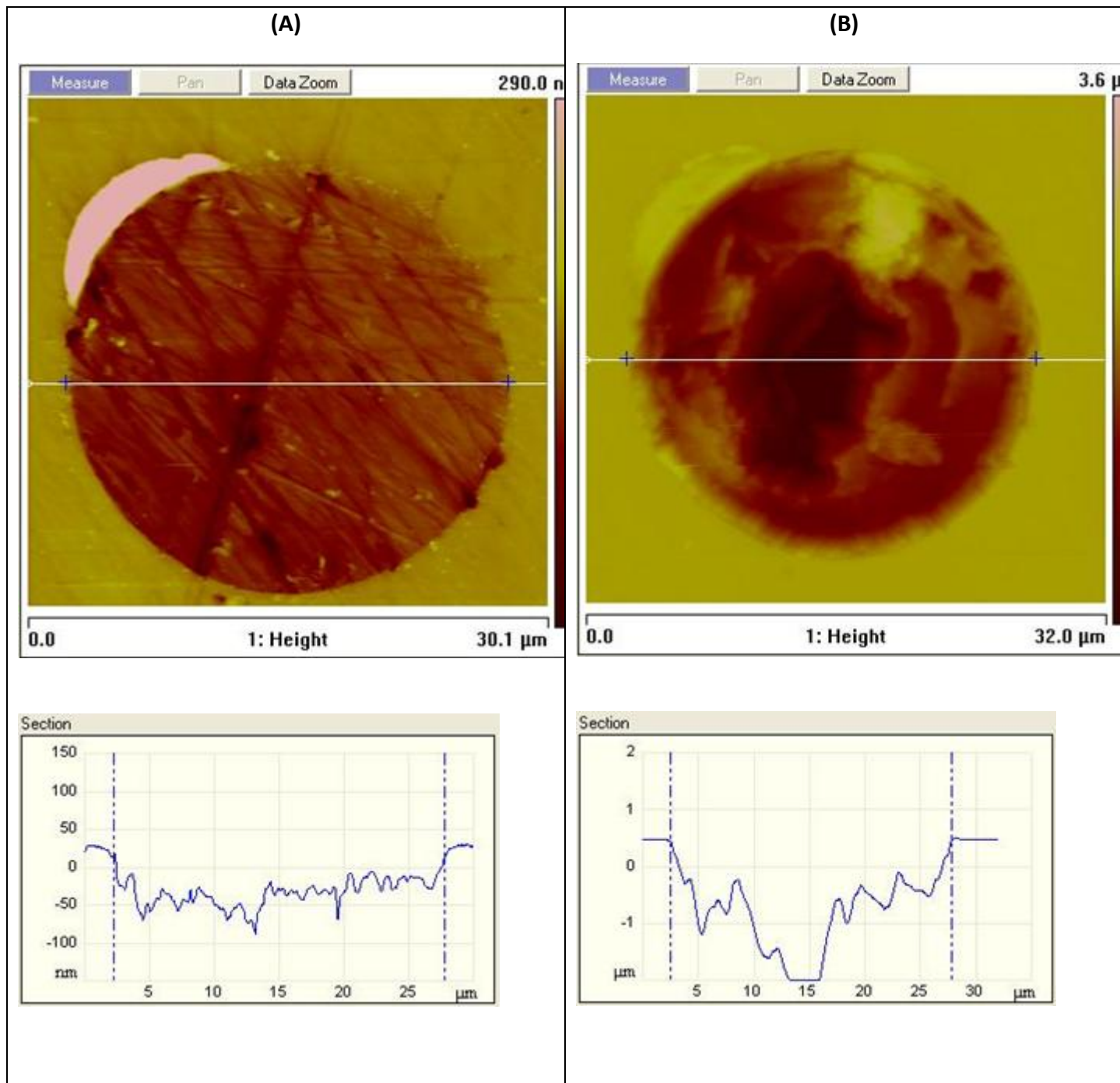


Figure S-5. AFM topography images with corresponding cross sections obtained for a platinum microelectrode. (A) – a fresh microelectrode; (B) – a microelectrode after 1 min. of ac modulation (0.3 V_{rms}, 0.1 MHz) in 0.2 M HCl at E_{dc} = 1.6 V vs. SCE.

Simulated cyclic voltammograms for an irreversible redox process

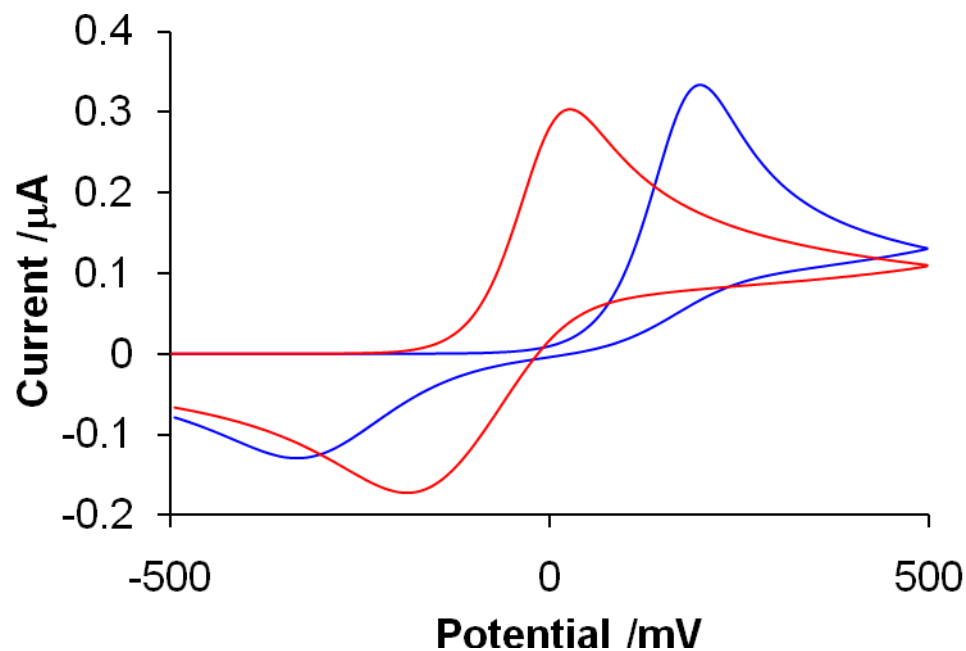


Figure S-6. Simulated cyclic voltammograms for a redox process with $E^\circ = 0$ mV, $k_s = 0.001$ cm/s, $\alpha = 0.65$ and the scan rate 20 V/s, with (red) and without (blue) superimposed ac modulation at frequency 100 kHz and amplitude 250 mV (peak to mean).

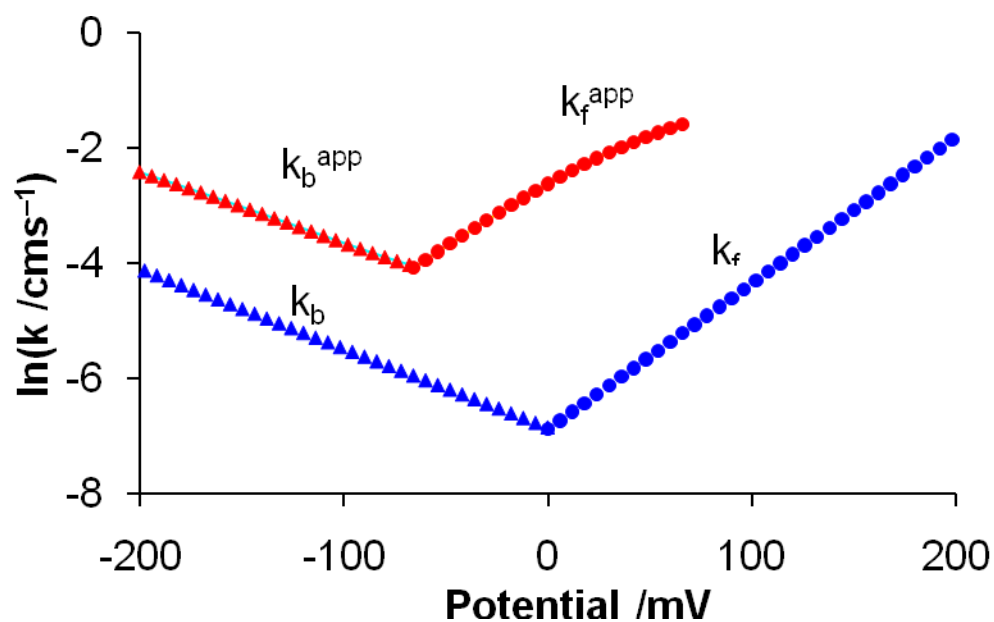


Figure S-7. Potential dependencies of the forward (k_f) and backward (k_b) electron transfer rate constants obtained from cyclic voltammograms in Figure S-6 by a convolution method.

Experimental steady-state voltammograms for the oxidation of $\text{Fe}(\text{CN})_6^{4-}$

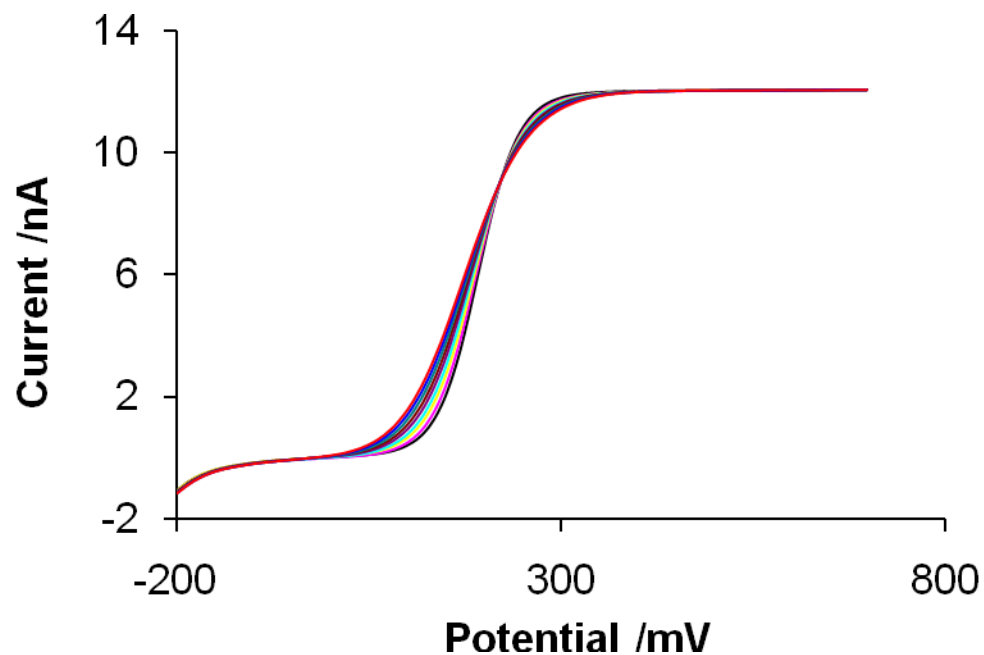


Figure S-8. Steady-state voltammograms for the oxidation of 20 mM $\text{Fe}(\text{CN})_6^{4-}$ in 2 M KCl and 40 mM KCN at a Pt disk microelectrode (3.6 μm in diameter). The scan rate was 0.01 V/s and the ac modulation of 10 MHz with amplitudes (in V_{rms}): 0 (black), 0.053, 0.075, 0.092, 0.107, 0.12, 0.13, 0.14 and 0.15 (red). Note that after accounting for the ohmic drop these amplitudes are about 25% smaller.

Simulated steady-state voltammograms (matching the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ on Pt)

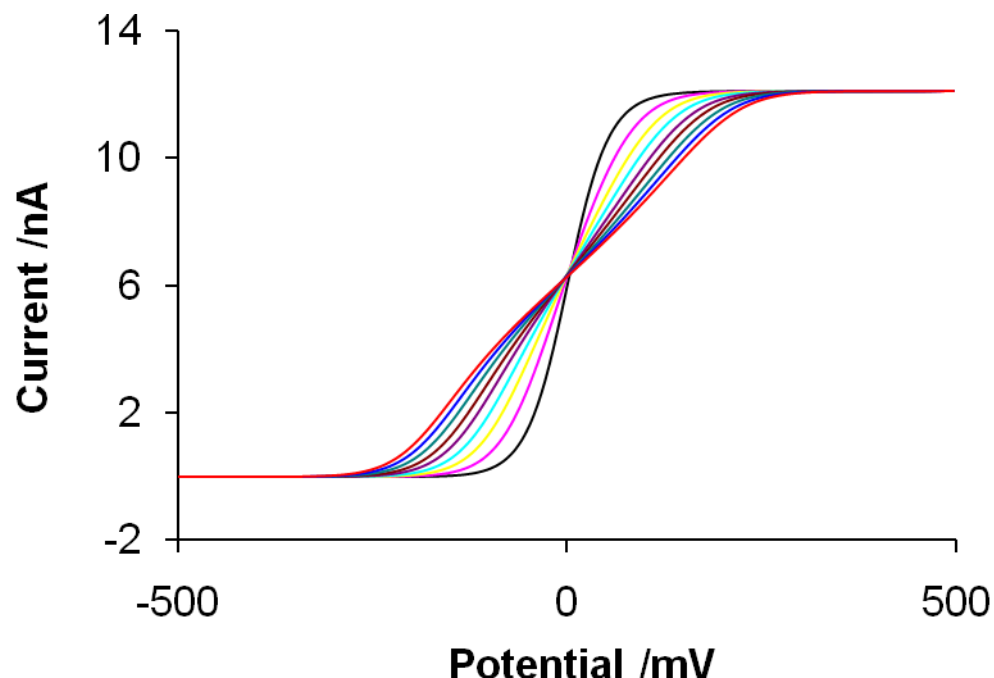


Figure S-9. Simulated steady-state voltammograms for a hemispherical electrode (2.5- μm in diameter) in the presence of the ac modulation of 0.1 MHz with amplitudes (in V_{rms}): 0 (black), 0.053, 0.075, 0.092, 0.107, 0.12, 0.13, 0.14 and 0.15 (red). Kinetic parameters of the electrode process: $\alpha = 0.6$, $d\alpha/dE = 0$ and $k_s = 1.5$ cm/s.

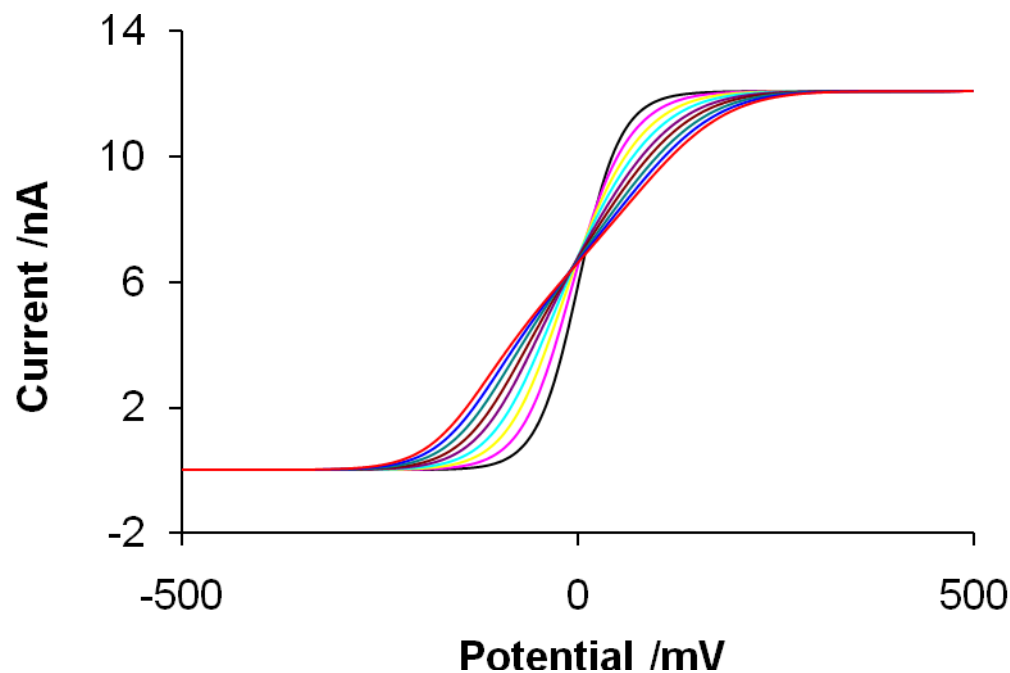


Figure S-10. Simulated steady-state voltammograms for a hemispherical electrode (2.5- μm in diameter) in the presence of the ac modulation of 1 MHz with amplitudes (in V_{rms}): 0 (black), 0.053, 0.075, 0.092, 0.107, 0.12, 0.13, 0.14 and 0.15 (red). Kinetic parameters of the electrode process: $\alpha = 0.6$, $d\alpha/dE = 0$ and $k_s = 1.5$ cm/s.

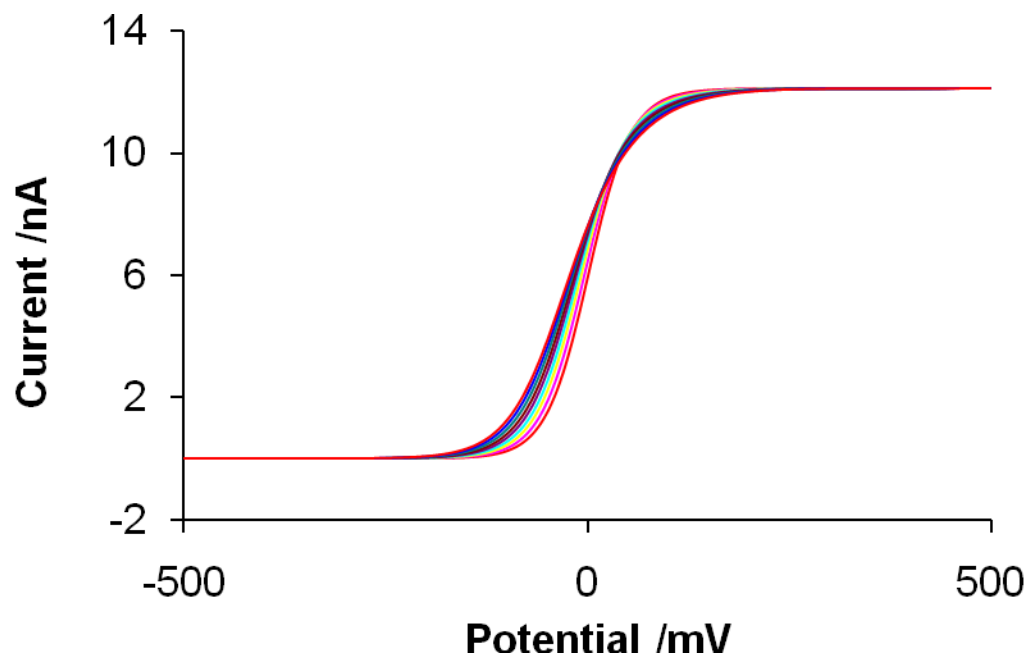


Figure S-11. Simulated steady-state voltammograms for a hemispherical electrode (2.5- μm in diameter) in the presence of the ac modulation of 10 MHz with amplitudes (in V_{rms}): 0 (black), 0.037, 0.053, 0.065, 0.075, 0.08, 0.09, 0.10 and 0.11 (red). Kinetic parameters of the electrode process: $\alpha = 0.6$, $d\alpha/dE = 0$ and $k_s = 1.5$ cm/s.