

Scheme 1
1

Surface electrode reaction

Multi-frequency electrochemical faradic spectroscopy

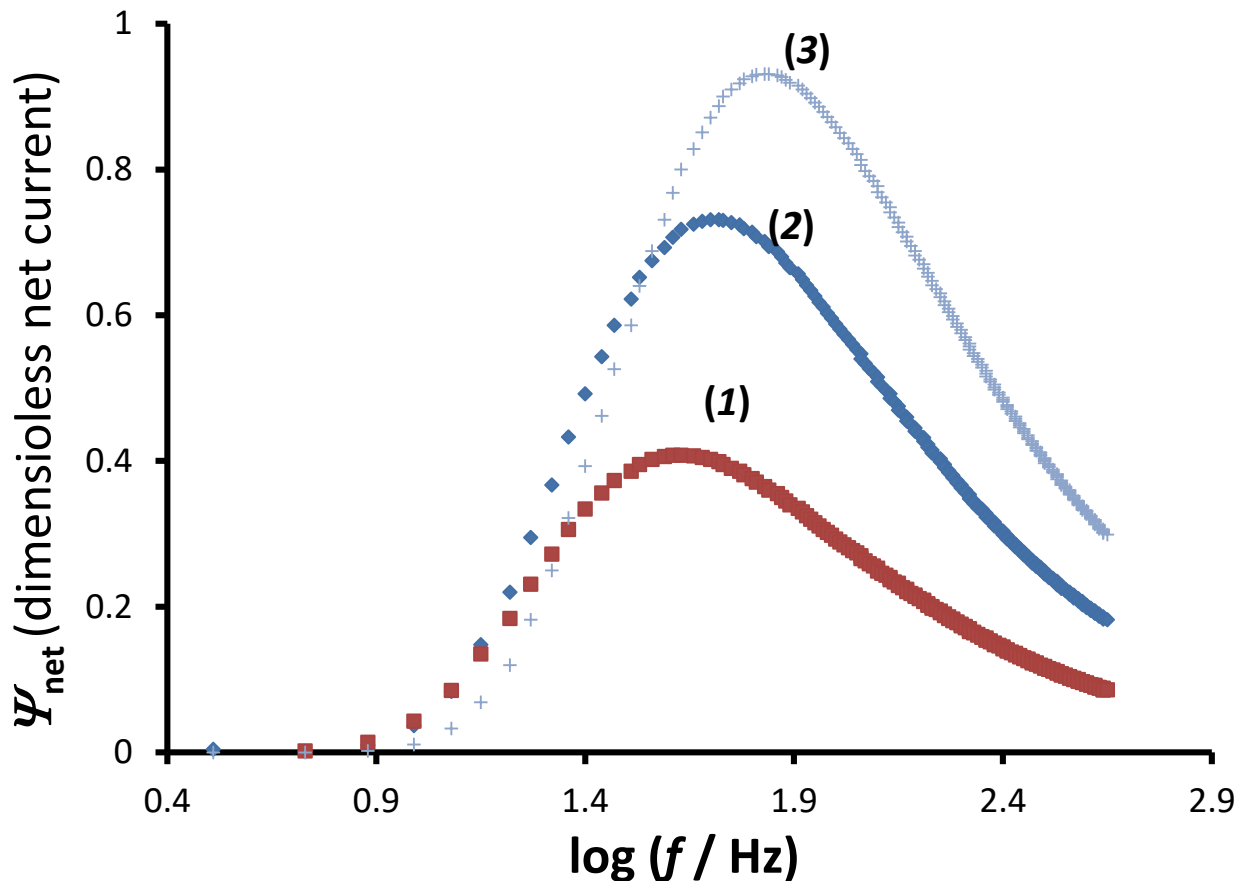
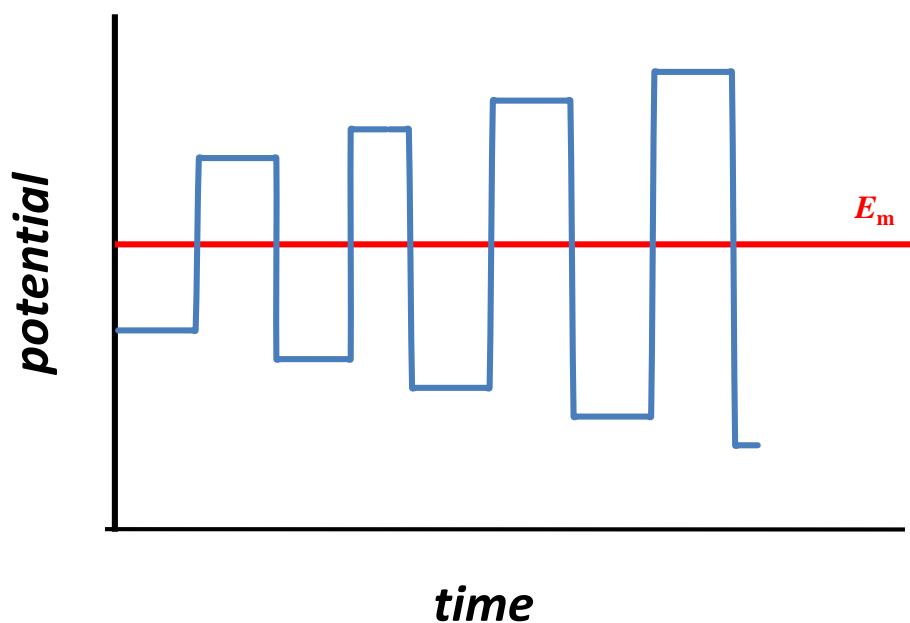


Fig. 1. Surface confined electrode reaction under conditions of multi-frequency variation in a single electrochemical faradaic spectroscopy experiment (MF-EFS). The effect of the SW amplitude on the frequency spectrum of the dimensionless net peak current for $k_{s,\text{sur}} = 51 \text{ s}^{-1}$. The amplitude values are $E_{\text{sw}} = 20$ (1); 40 (2) and 60 mV (3). The frequency increases from 3 Hz to 887 Hz with an increment of 2 Hz. The other conditions are: electron transfer coefficient $\beta = 0.5$, $n = 1$, $T = 298.15$ K, and mid-potential $E_m = 0 \text{ V}$ vs $E^{0'}$

Multi-amplitude electrochemical faradaic spectroscopy (MA-EFS)



Scheme 2

Multi-amplitude electrochemical faradic spectroscopy

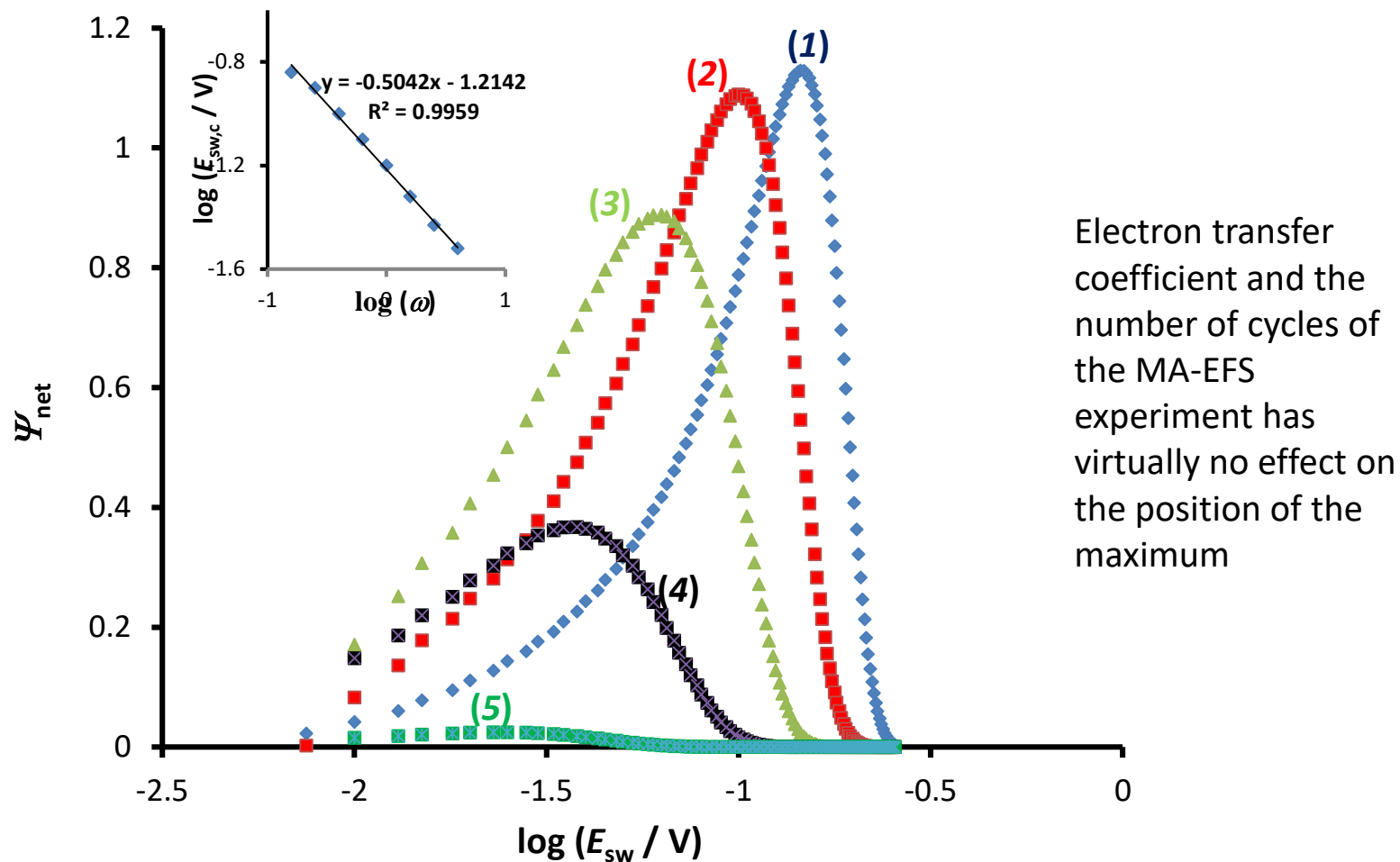
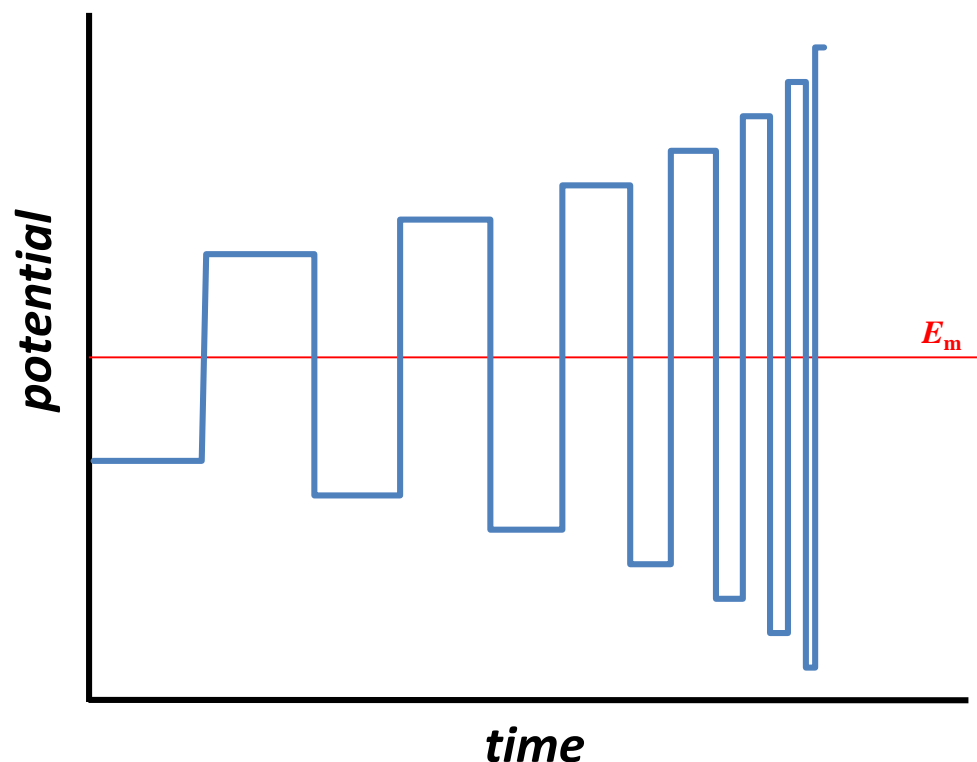


Fig. 2. Surface confined electrode reaction under conditions of multi-amplitude variation in a single electrochemical faradaic spectroscopy experiment (MA-EFS) for different electrochemical reversibility. The values of the electrode kinetic parameter ($w = k_s/f$) are: $\log(w) = -0.8$ (1); -0.4 (2); 0 (3); 0.4 (4) and 0.8 (5). The other conditions are: electron transfer coefficient $\beta = 0.5$, $n = 1$, $T = 298.15$ K, and $E_m = 0$ V vs $E^{0'}$.

Multi-frequency-multi-amplitude electrochemical faradaic spectroscopy (MFA-EFS)



Scheme 3

Multi-frequency-multi-amplitude electrochemical faradic spectroscopy

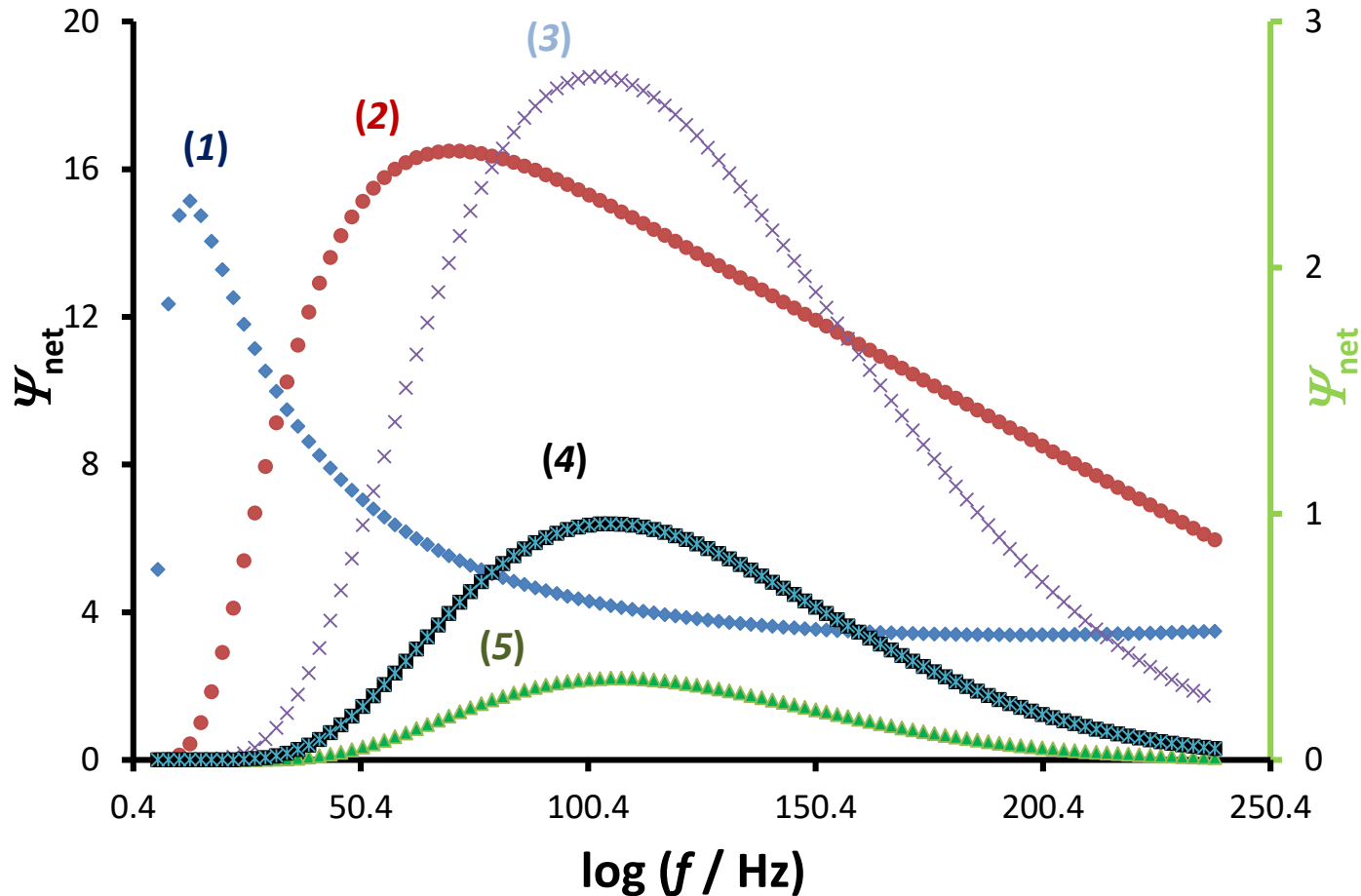


Fig. 3. Surface confined electrode reaction under conditions of multi-amplitude and multi-frequency variation in a single electrochemical faradaic experiment (MFA-EFS). The values of the standard rate constant are: $k_s = 10$ (1); 100 (2); 300 (3); 400 (4) and 500 s^{-1} (5, left ordinate). The SW chronoamperometric program contains 100 potential cycles varying progressively the SW amplitude from 7.5 to 130 mV with an increment of 1.25 mV and the frequency from 5.7 to 238 Hz with an increment of 2.4 Hz. The other conditions are: electron transfer coefficient $\beta = 0.5$, $n = 1$, $T = 298.15 \text{ K}$, and $E_m = 0 \text{ V}$ vs $E^{0'}$.

Experimental data and fitting: Azobenzene at HMDE

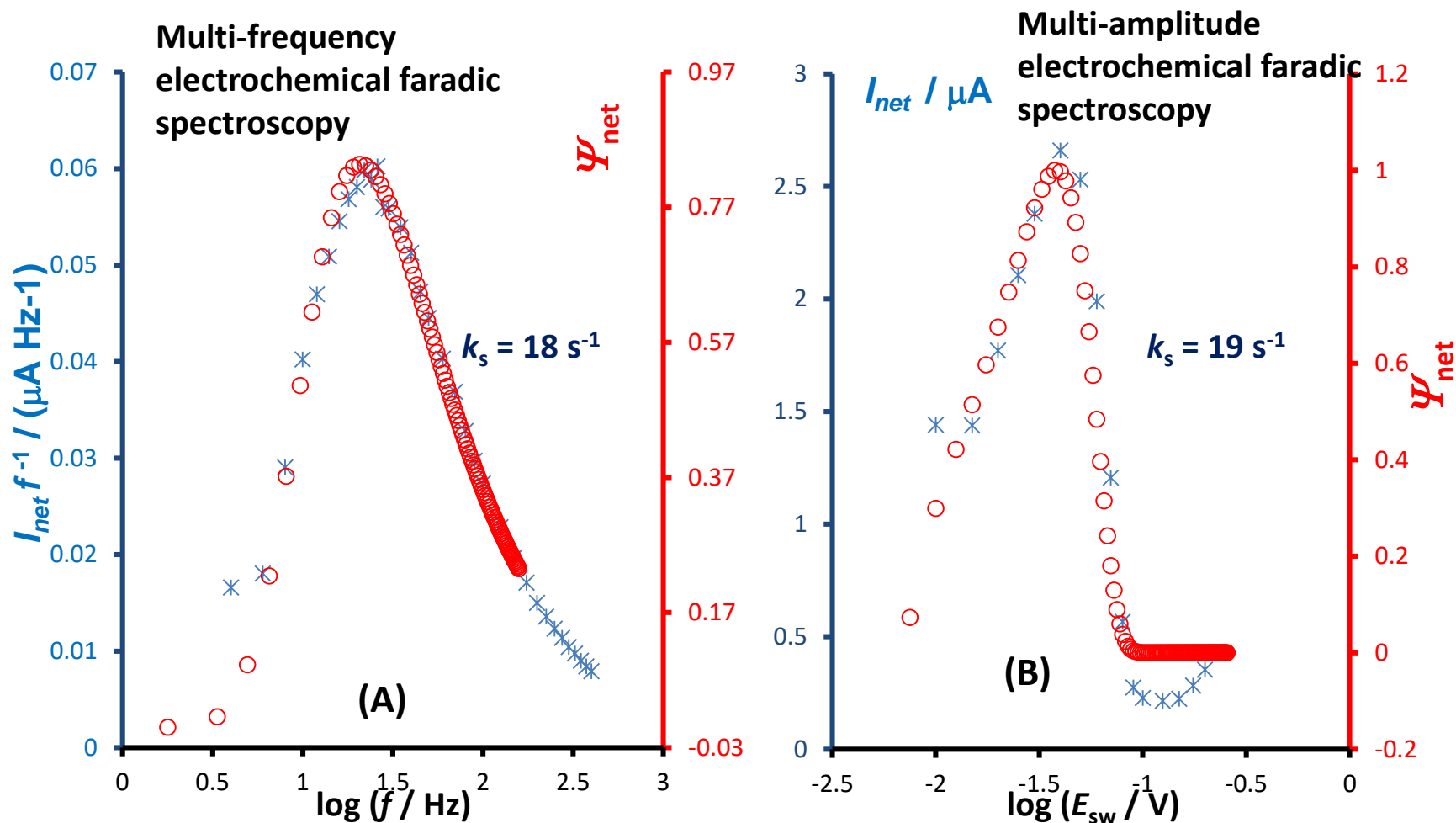


Fig. 4. Azobenzene electrode reaction at HMDE in a phosphate buffer at pH = 5, at concentration of $c = 2 \text{ mmol/L}$, with accumulation time of 60 s at potential of 0.00 V. **(A)** Multi-frequency analysis. Frequency spectrum of experimental (blue asterisks, left ordinate) and theoretical data (red circles, right ordinate), simulated for standard rate constant $k_s = 18 \text{ s}^{-1}$ and amplitude of $E_{\text{sw}} = 25 \text{ mV}$. **(B)** Multi-amplitude analysis. Amplitude spectrum of experimental (blue asterisks, left ordinate) and theoretical data (red circles, right ordinate), simulated for standard rate constant $k_s = 19 \text{ s}^{-1}$ and frequency of $f = 25 \text{ Hz}$. The other conditions of simulations for both panes are: electron transfer coefficient $\beta = 0.5$, number of electrons $n = 2$, temperature $T = 298.15 \text{ K}$, and number of potential cycles $p = 100$.