Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Electrode kinetics from a single experiment: Multi-amplitude analysis in square-wave chronoamperometry

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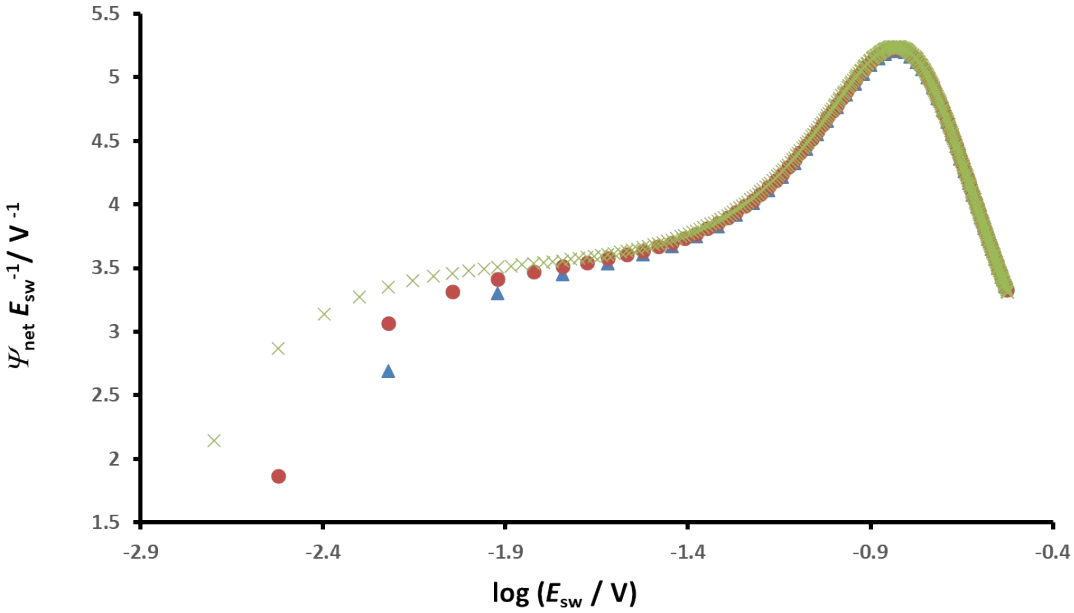

Fig. S1. Theoretical simulations in MA-SWCA for a quasireversible electrode reaction of a dissolved redox couple showing the effect of the amplitude increment in the amplitude-based quasireversible maximum. The values for the amplitude increment are: ΔE_{sw} = 1 mV (asterisks), 3 mV (circles) and 6 mV (triangles). The other conditions are identical as for Fig. 2 (A).

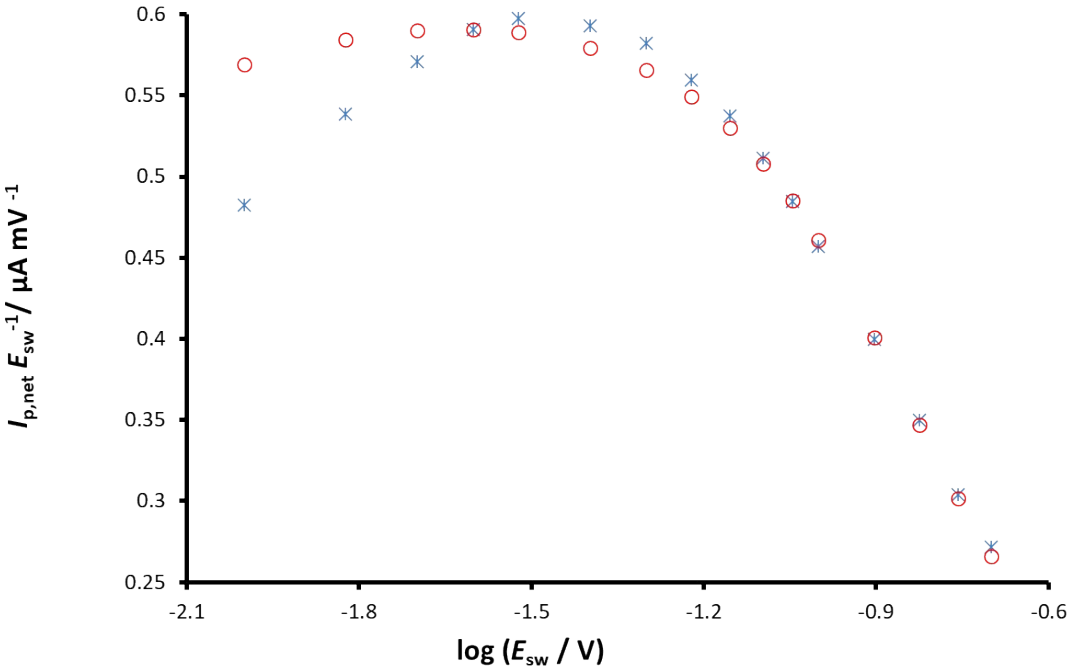

Fig. S2. Fitting of the theoretical and experimental data of the amplitude-based quasireversible maximum in SWV for a hexacyanoferrate redox system in 0.1 mol/L KNO_3 supporting electrolyte at a glassy carbon electrode. Experimental (asterisks) and theoretical data (circles), simulated for the standard rate constant k_s = 5.0 × 10^{-3} cm s^{-1}; diffusion coefficient D = 5 × 10^{-6} cm^2 s^{-1}; anodic electron transfer coefficient α = 0.55; amperometric constant A = 54 µA ($A = I / \Psi$), and temperature T = 291.15 K. The other conditions for both theory and experiment are: frequency f = 25 Hz; bulk concentration of both $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ is c = 0.25 mmol/L and the step potential increment ΔE = 5 mV**.**

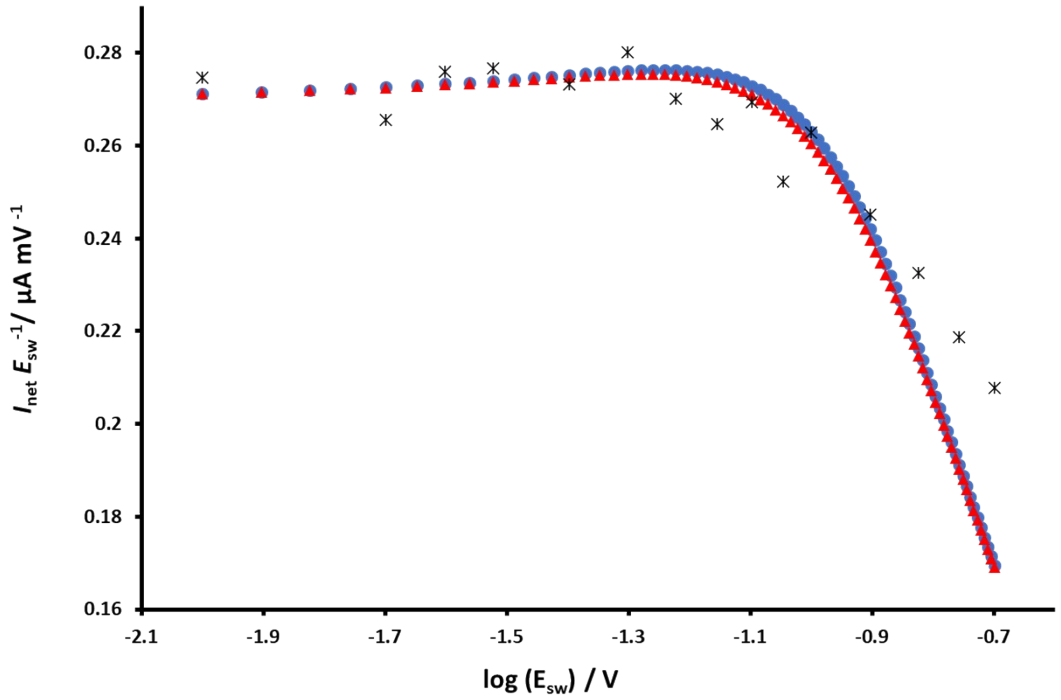

Fig. S3. Fitting of the theoretical (circles and triangles) and experimental data (asterisks) of the amplitude-based quasireversible maximum in MA-SWCA for a hexacyanoferrate redox system in 0.1 mol/L KNO_3 supporting electrolyte at a glassy carbon electrode. Theoretical data are simulated for different anodic electron transfer coefficients α = 0.45 (red triangles) and α = 0.50 (blue circles), with the standard rate constant k_s = 3.0 × 10^{-3} cm s^{-1}, and amperometric constant A = 3,4 × 10^{-5} A (the values for α = 0.55 are virtually identical as for α = 0.45). The other conditions for both theory and experiment are identical as in Fig. S2.