

# Double-sampled differential square-wave voltammetry-Supplementary Information

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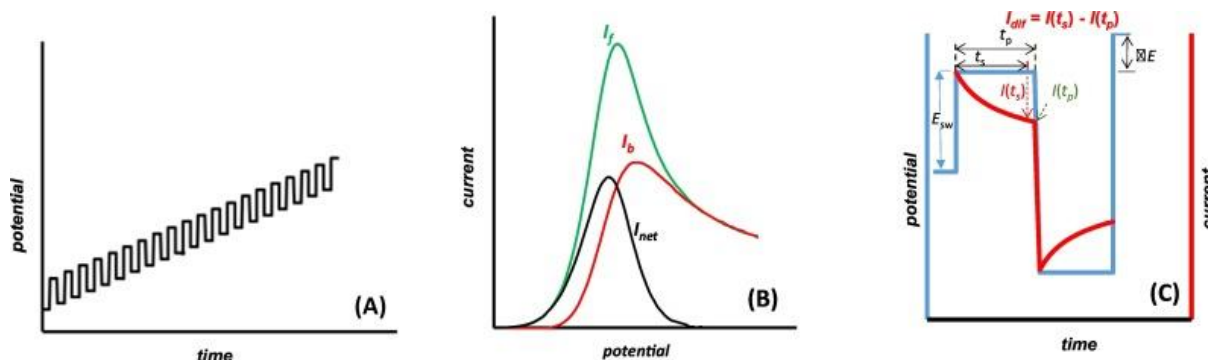
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## Supplementary information

**Fig. S1 (A)** Quasireversible electrode reaction of a dissolved redox couple at a planar macroscopic electrode. The dependence of the peak current ratio ( $I_{p,f}/I_{p,b}$ ) on the sampling time ratio ( $t_s/t_p$ ) in DSSWV for standard rate constant of  $\log(k_s/\text{cm s}^{-1}) = -3.3$  (1); -2.7 (2) and -1.7 (3) and frequency of 10 Hz. **(B)** The dependence of the peak current ratio in DSSWV (left ordinate, curves 1 and 2) and normalized real net peak current ( $\Delta \Psi_{pf}^{0.5}$ ) in conventional SWV (right ordinate, curve 3) on the SW frequency. The simulations for the date of curve (1) correspond to the sampling time ratio  $t_s/t_p$

varying from 0.8 to 0.9 and the standard rate constant of  $k_s = 1 \times 10^{-2} \text{ cm s}^{-1}$  while the curve (2) correspond to  $k_s = 0.8 \times 10^{-2} \text{ cm s}^{-1}$  and  $t_s/t_p = 0.8$ . The standard rate constant for curve (3) is  $k_s = 1 \times 10^{-2} \text{ cm s}^{-1}$ . The other conditions of the simulations for both panels are:  $E_{sw} = 25 \text{ mV}$ ,  $\Delta E = 5 \text{ mV}$ ,  $\beta = 0.5$ ,  $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , and  $T = 298.15 \text{ K}$ .

**Fig. S2.** Quasi-reversible electrode reaction of a dissolved redox couple at a planar macroscopic electrode. Amplitude based quasi-reversible maximum. The dependency of the amplitude normalized net peak current on the SW amplitude for DSSWV (circles, right ordinate) and conventional SWV (squares, left ordinate) for  $\log(\kappa) = -0.1$ ,  $\beta = 0.5$ , and time sampling ratio  $t_s/t_p = 0.7$ . The other conditions are the same as for Fig. S1.

**Fig. S3.** Quasi-reversible electrode reaction of a dissolved redox couple at a planar macroscopic electrode. The effect of the electrode kinetic parameter  $\kappa$  for different variants of SWV, including electrochemical faradaic spectroscopy (1) [4], differential square-wave voltammetry (2) [7], conventional square-wave voltammetry (3) and the present double-sampled differential square-wave voltammetry (4). Curves (1-3) refer to the net peak current of corresponding techniques plotted on the left ordinate, while curve (4) refers to the forward-to-backward peak current ratio of DSSWV plotted on the right ordinate. The time sampling ratio for double-sampled differential square-wave voltammetry (curve 4) and the step-to-pulse duration ratio for differential square-wave voltammetry (curve 2) is 0.82. The other conditions of the simulations for all techniques are:  $E_{sw} = 50 \text{ mV}$ ,  $\Delta E = 10 \text{ mV}$ ,  $\beta = 0.5$ , and  $T = 298.15 \text{ K}$ .

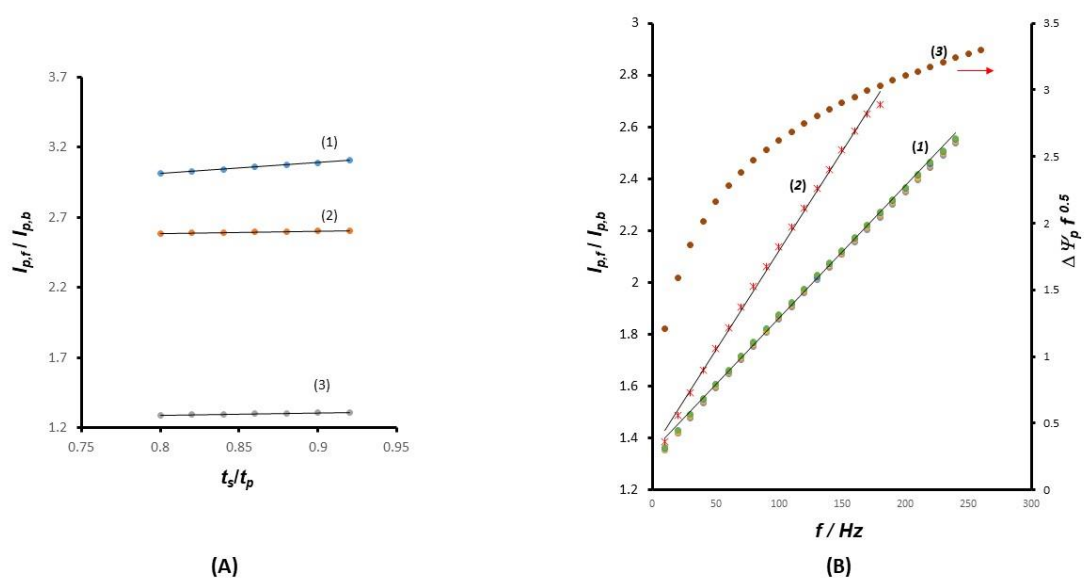


Fig. S1

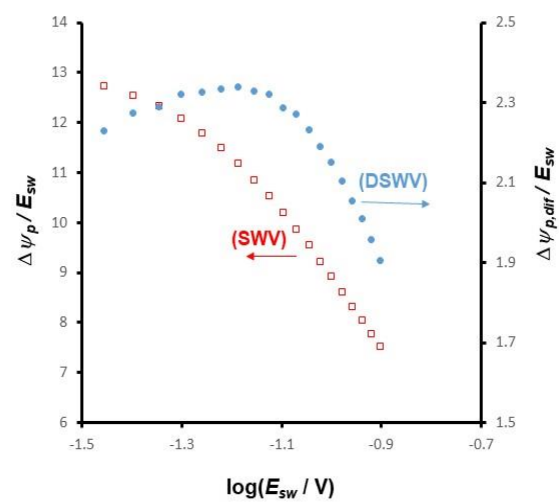


Fig. S2

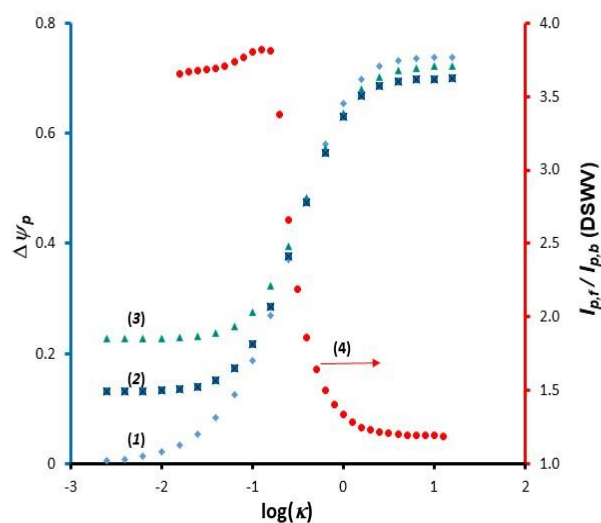


Fig. S3

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