# Diffusional EC’ Mechanism-Applying a differentiation method to transform steady state to peaks form cyclic voltammograms

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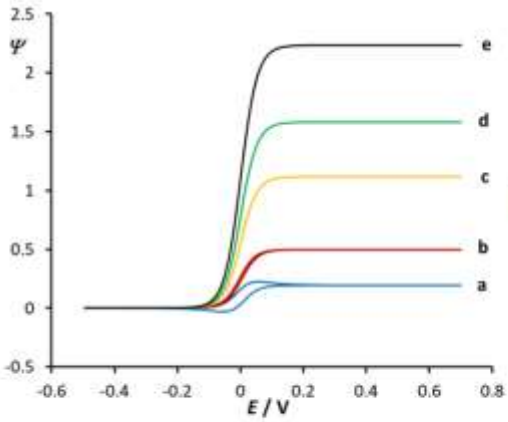
## Abstract

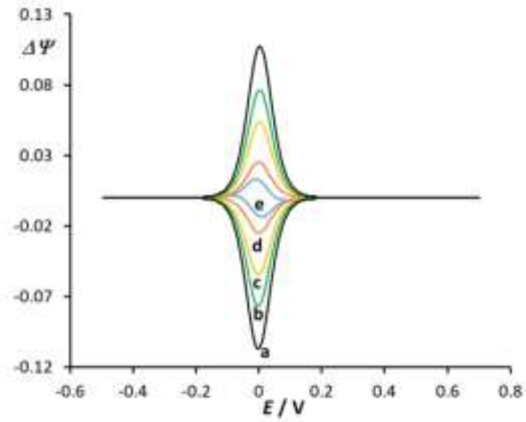
The diffusional EC′ mechanism is one of the fundamental reaction schemes in electrochemical kinetics, describing an electron-transfer step followed by a regenerative chemical reaction that restores the electroactive species. At sufficiently high rates of the regenerative reaction, the voltammetric response progressively changes from a conventional peak-shaped profile toward a sigmoidal, steady-state-like catalytic wave. Although this behavior represents a characteristic signature of efficient regeneration, the absence of a well-defined current maximum limits the applicability of conventional peak-based methods for quantitative kinetic analysis. In this work, we introduce a simple differentiation approach for transforming steady-state-like voltammograms of the diffusional EC′ mechanism into well-defined peak-shaped responses. The method is based on calculating the difference between currents measured at two consecutive potential points and normalizing this difference by the potential increment, providing a discrete approximation of the first derivative of the voltammetric response. Numerical simulations demonstrate that differentiation converts the sigmoidal catalytic wave into a distinct peak whose position, magnitude, and shape systematically depend on the kinetics of the regenerative chemical reaction. Consequently, kinetic information that is difficult to extract directly from the original steady-state response becomes accessible through measurable peak parameters. The proposed approach provides an alternative strategy for evaluating regenerative reaction kinetics and extends the analytical utility of voltammetric measurements for diffusional EC′ systems.

Ket = 100---very fast
dE = 10 mV
Tau = 0.05

Kcat = 0.038 (a); 0,25 (b); 1.25 (c); 2.5 (d); 5 (e)

$$\Delta\Psi_p := \Psi_p - \Psi_{p-1}$$

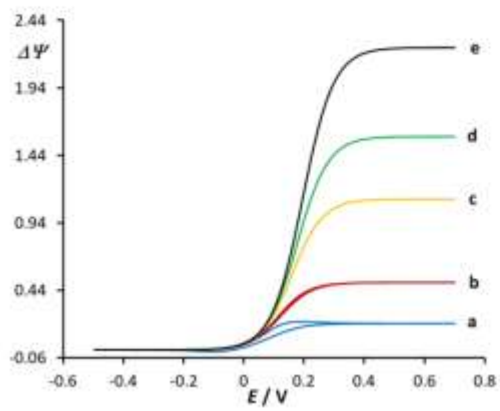


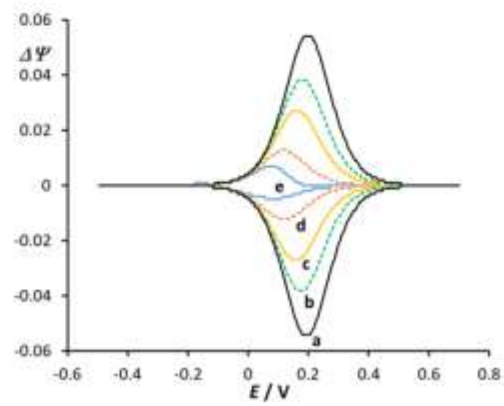




Ket = 0.05--quasireversible
dE = 10 mV
Tau = 0.05

Kcat = 0.038 (a); 0,25 (b); 1.25 (c); 2.5 (d); 5 (e)

$$\Delta\Psi_p := \Psi_p - \Psi_{p-1}$$

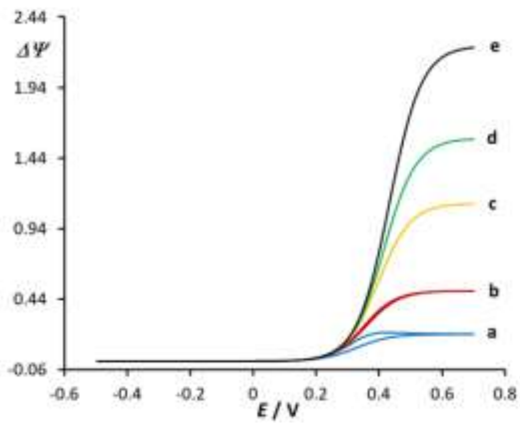


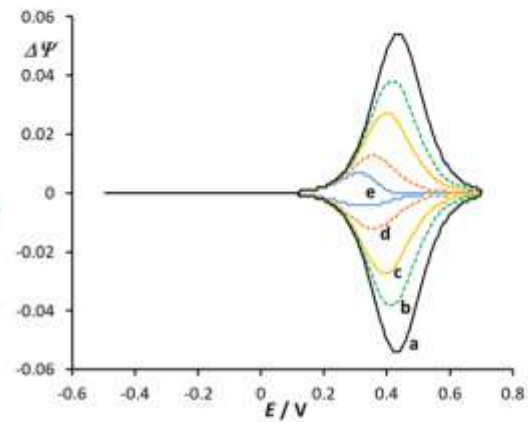



Ket = 0.0005-irreversible
dE = 10 mV
Tau = 0.05

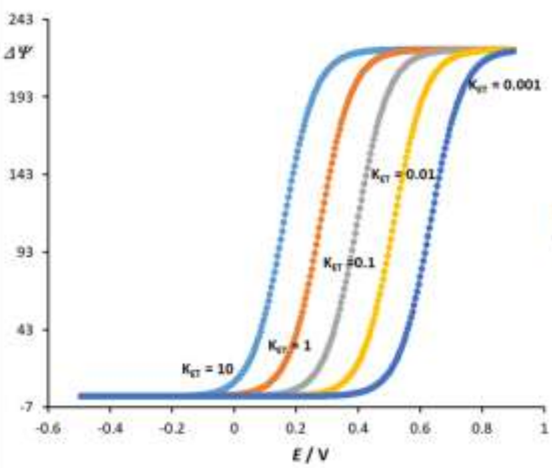
Kcat = 0.038 (a); 0,25 (b); 1.25 (c); 2.5 (d); 5 (e)

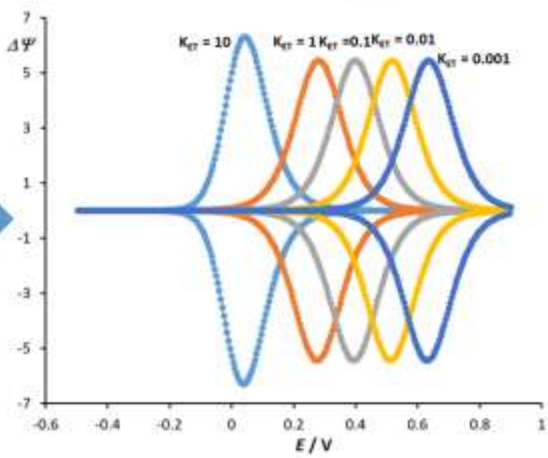
$$\Delta\Psi_p := \Psi_p - \Psi_{p-1}$$

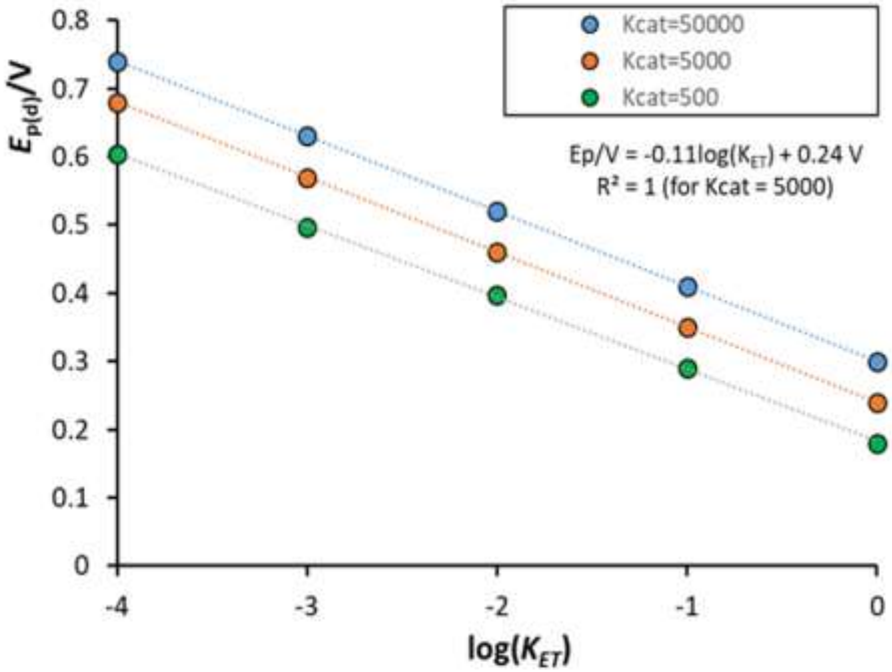


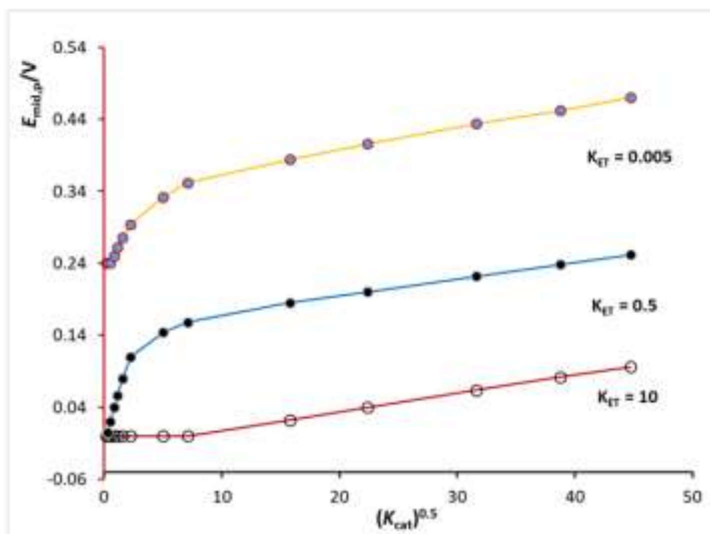

**Differencijalni Voltamogrami od EC' difuzionen Pri znacitelna Kataliza od Kcat = 5000**

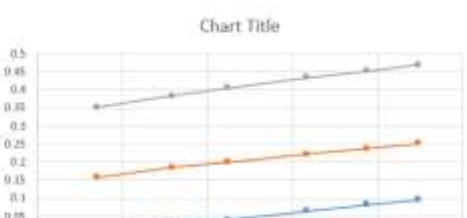





Mid-peak potential (Emid,p)
vs. square-root of Kcatalytic
At fat, modest and slow
Electron transfer



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