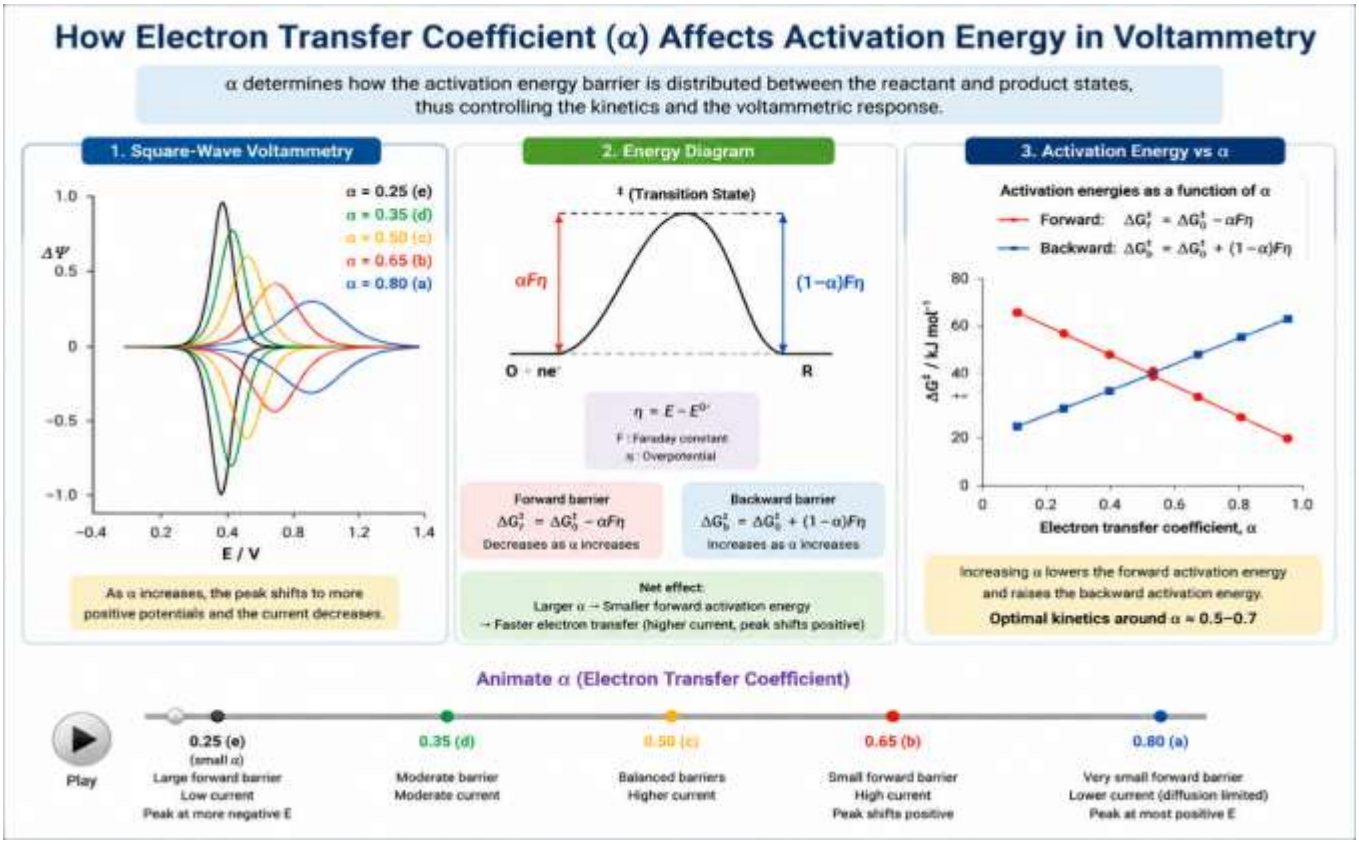
Electron transfer coefficient influence to the differential voltammograms of an EC’ mechanism in cyclic voltammetry

Pavle Apostoloski, Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

Abstract

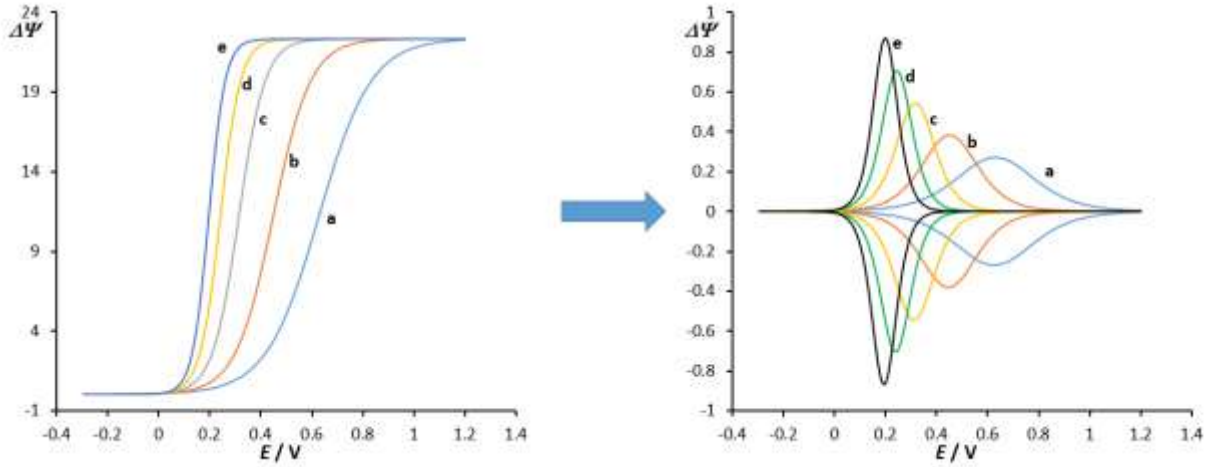
The electron-transfer coefficient, α, is a fundamental kinetic parameter describing the symmetry of the activation-energy barrier and its response to the applied electrode potential. In this work, the influence of α on the differential voltammetric response of a diffusional EC’ mechanism in cyclic voltammetry is investigated theoretically. Conventional catalytic voltammograms were transformed into peak-shaped differential responses by calculating the current difference between consecutive potential points. Systematic variation of α revealed pronounced changes in both the magnitude and position of the differential peaks. Increasing α progressively decreased the forward differential peak current while shifting its peak potential toward more positive values. Within the investigated range, both quantities exhibited well-defined nonlinear dependences on the electron-transfer coefficient, which could be approximated by exponential functions. These features originate from the influence of α on the potential-dependent activation barrier of the heterogeneous electron-transfer step and its interplay with the regenerative chemical reaction. The results demonstrate that differential transformation considerably enhances the visibility of kinetic effects that are less apparent in the original steady-state-like catalytic voltammograms. Consequently, the differential EC’ approach provides a simple framework for evaluating the influence of the electron-transfer coefficient and may facilitate extraction of kinetic information from catalytic cyclic voltammetric responses.

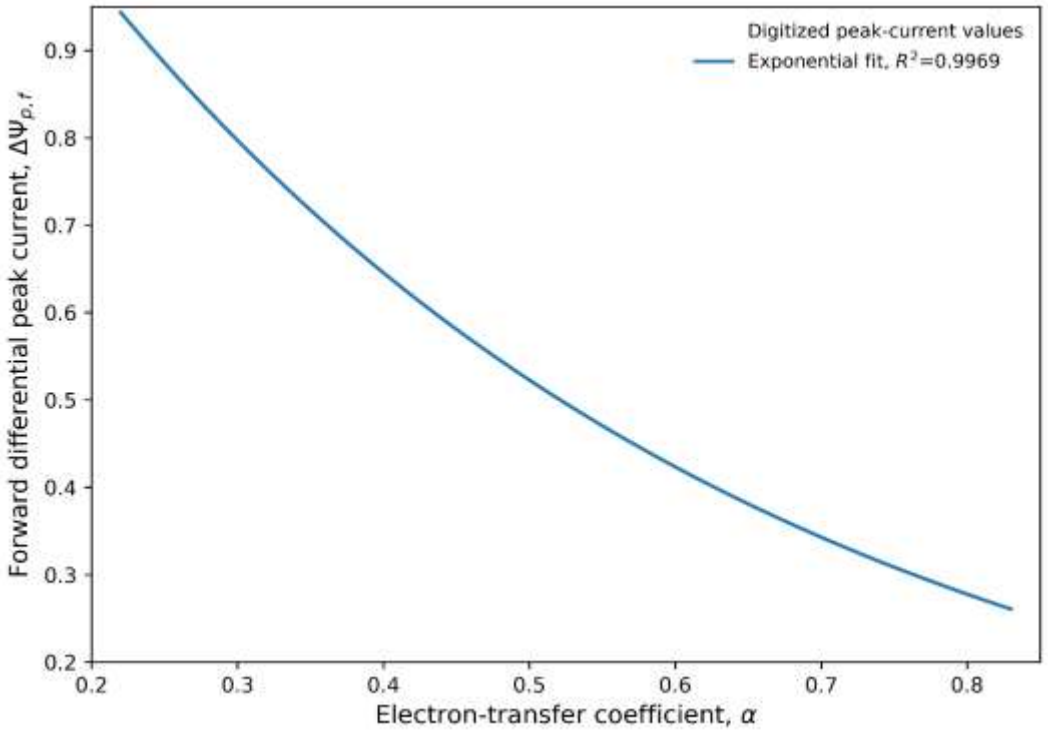


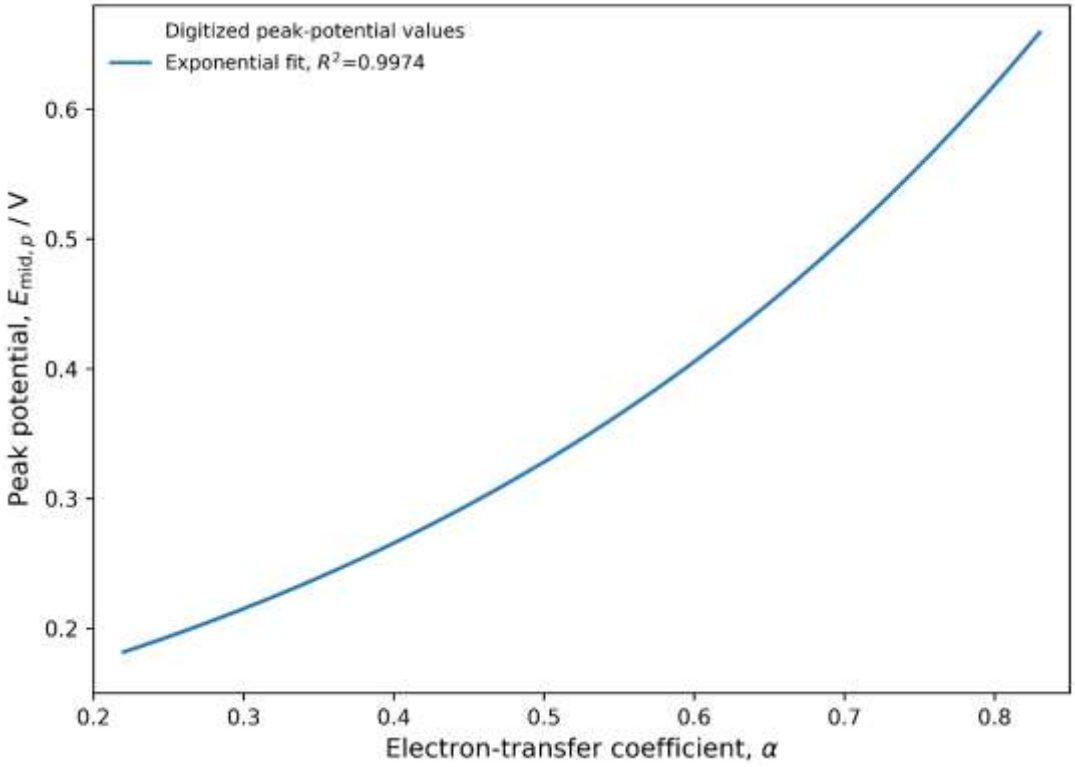
Real (left) and differential (right) voltammograms of diffusional EC′ mechanism in Cyclic voltammetry=effect of electron transfer coefficient

K=0.05
dE=10
D=5x10^-6
tau=0.05
Kcat=500

Alpha = 0.25 (a); 0.35 (b); 0.5 (c) 0.65 (d) and 0.8 (e)




Digitized peak-current values
Exponential fit, R^2=0.9969
Forward differential peak current, $\Delta\Psi_{p,f}$
Electron-transfer coefficient, α
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9


Digitized peak-potential values
Exponential fit, R^2=0.9974
Peak potential, $E_{mid,p}$ / V
Electron-transfer coefficient, α
0.2
0.3
0.4
0.5
0.6
0.7
0.8

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