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Higher order derivative voltammetry for reversible and irreversible electrode processes under spherical diffusion

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Theoretical expressions for the first, second and third derivatives of voltammetric curves are analytically derived for reversible, quasi-reversible, and irreversible processes under spherical diffusion. The shapes of the curves are analyzed in terms of peak-potentials, peak-currents, and peak-widths, and the differences and ratios among them. The results obtained with spherical electrodes are compared with those with the planar electrodes, which exhibits striking differences between two electrodes. Derived parameters – such as ratios of peak-currents (i^a_p/i^c_p), and ratios of half-peak-widths ($W^a_{½}/W^c_{½}$), and ratios of the differences in peak potentials ($\Delta E^a_p/\Delta E^c_p$), for various derivatives are analyzed. As electrode sphericity increases, these ratios (i.e., measures of symmetry in the curves) for a quasi-reversible and irreversible electron transfer process approaches to one, which is the same as that for a simple reversible electrode process on a planar electrode. Namely, the asymmetry which was exhibited on planar electrodes for quasi and irreversible processes disappears on a spherical electrode. This suggests that the planar electrode is better suited for kinetic study of slower electron transfer than spherical electrodes for this derivative approach.

Biography

Iason Rusodimos has completed his BS in Electrical Engineering (1976), MS in Electrical Engineering (1977), MS in Math (1983), MS in Physics (1984), all from the Georgia Institute of Technology. Since 1986, he joined the Faculty of Georgia Perimeter College, which has been recently consolidated with Georgia State University, teaching mostly Calculus, Differential Equations, and Linear Algebra courses. In addition to developing various instructional methods associated with STEM education, he has long been interested in effective applications of Math to Science and Engineering. Recently, he has been interested in application of derivatives approach in Science and Engineering, in kinetic processes, as illustrated in this presentation. Major area of research has been solving partial differential equations on a physical or mechanical system associated with elasticity, and on chemical systems of heterogeneous electron-transfer kinetics.

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