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HIGHER ORDER DERIVATIVE VOLTAMMETRY FOR REVERSIBLE AND IRREVERSIBLE ELECTRODE PROCESSES UNDER SPHERICAL DIFFUSION

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ABSTRACT

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 n 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_p^a/i_p^c), and ratios of half-peak-widths ($W_{½}^a/W_{½}^c$), and ratios of the differences in peak potentials ($\Delta E_p^a/\Delta E_p^c$), 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 suggest that the planar electrode is better suited for kinetic study of slower electron transfer than spherical electrodes for this derivative approach.

Key Words: Derivative Voltammetry, Heterogeneous Kinetics, Spherical Electrodes