

## Accepted Manuscript

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PII: S1572-6657(16)30715-9  
DOI: doi: [10.1016/j.jelechem.2016.12.022](https://doi.org/10.1016/j.jelechem.2016.12.022)  
Reference: JEAC 3018

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 14 September 2016  
Revised date: 9 December 2016  
Accepted date: 12 December 2016

Please cite this article as: Tae-Kee Hong, Iason Rusodimos, Myung-Hoon Kim , Higher order derivative voltammetry for reversible and irreversible electrode processes under spherical diffusion. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Jeac(2016), doi: [10.1016/j.jelechem.2016.12.022](https://doi.org/10.1016/j.jelechem.2016.12.022)

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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 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 ( $i_p^a/i_p^c$ ), and ratios of half-peak-widths ( $W_{1/2}^a/W_{1/2}^c$ ), 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 suggests 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

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