Highly accurate, efficient, and automatic computation of reversible cyclic voltammograms, using double exponential formulas for numerical integration

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PII: S1572-6657(17)30871-8
DOI: doi:10.1016/j.jelechem.2017.11.069
Reference: JEAC 3699

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 10 October 2017
Revised date: 25 November 2017
Accepted date: 27 November 2017

Please cite this article as: L.K. Bieniasz, Highly accurate, efficient, and automatic computation of reversible cyclic voltammograms, using double exponential formulas for numerical integration, *Journal of Electroanalytical Chemistry* (2017), doi:10.1016/j.jelechem.2017.11.069

Highly accurate, efficient, and automatic computation of reversible cyclic voltammograms, using double exponential formulas for numerical integration

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Abstract

Highly accurate reference values of theoretical cyclic voltammograms are indispensable for those who develop and examine simulation methods or other modelling approaches for electroanalytical chemistry. Reference values having relative errors close to $\pm 10^{-16}$ (which is the level of the representation errors of standard double precision variables) are desirable, but they cannot be obtained efficiently using conventional simulations. A class of reversible cyclic voltammograms can be expressed in terms of improper convolution integrals that have to be evaluated numerically. By employing the efficient automatic numerical integration package INTDE of Ooura, based on double exponential formulas, and written in "C", it is shown that such voltammograms can be calculated with relative errors close to $\pm 10^{-16}$, in a time of ca. 1 ms per single current function value, on a contemporary laptop computer. Furthermore, this method appears resistant to failures that may accompany highly accurate numerical integration by alternative methods and software. This is demonstrated for three kinetic examples under conditions of pure diffusion transport: reversible charge transfer at a planar electrode; reversible charge transfer at a spherical electrode; and $E_{rev}C_{irr}$' mechanism at a planar electrode.

Keywords: computational electrochemistry, cyclic voltammetry, Randles-Ševčik function, double exponential quadratures, accurate computing

1. Introduction

Cyclic voltammetry belongs to the most commonly used controlled-potential transient electroanalytical techniques [1]. Consequently, there is a systematic need to compute theoretical cyclic voltammograms (CVs) corresponding to a variety of kinetic models. Unfortunately, analytical formulae describing CVs

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