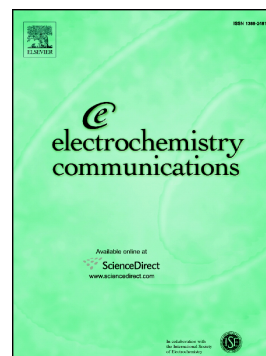


Accepted Manuscript

Analysis of quasi-reversible cyclic voltammograms:
Transformation to scan-rate independent form

Tamás Pajkossy



PII: S1388-2481(18)30074-2
DOI: doi:[10.1016/j.elecom.2018.04.004](https://doi.org/10.1016/j.elecom.2018.04.004)
Reference: ELECOM 6180
To appear in: *Electrochemistry Communications*
Received date: 21 March 2018
Revised date: 4 April 2018
Accepted date: 5 April 2018

Please cite this article as: Tamás Pajkossy , Analysis of quasi-reversible cyclic voltammograms: Transformation to scan-rate independent form. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. *Elecom*(2017), doi:[10.1016/j.elecom.2018.04.004](https://doi.org/10.1016/j.elecom.2018.04.004)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Analysis of quasi-reversible cyclic voltammograms: transformation to scan-rate independent form

Tamás Pajkossy

Institute of Materials and Environmental Chemistry

Research Centre for Natural Sciences, Hungarian Academy of Sciences

Magyar tudósok körútja 2, Budapest, Hungary, H-1117

e-mail: pajkossy.tamas@ttk.mta.hu

Abstract

A simple procedure is suggested by which cyclic voltammograms, CVs, pertaining to partially diffusion controlled charge transfer reactions can be analyzed. Using this procedure, from a set of CVs taken at varied scan rates, two scan-rate independent, hysteresis-free functions can be calculated. One of them is the diffusion-free polarization curve, the other is the semiintegrated form of the reversible CV.

Keywords: diffusion, charge transfer, semiintegration, kinetics, redox system

1. Introduction

Cyclic voltammetry (CV) is a widely used experimental method for studying kinetics of electrode processes: the current density, as a function of time, $j(t)$ is measured as a function of time-varying potential, $E(t)$. The latter is scanned between two limits with constant speed, $v = dE/dt$; the CVs are the $j(E)$ curves. Both $j(t)$ and $j(E)$ are complicated functions of v ; hence comparison of two CVs measured with different v is far from being trivial.

In rare, simple cases, however, there exist mathematical transformations by which CVs taken with different scan rates can be transformed to the one-and-the-same $T(E)$ function – which function does not “remember” the actual form of $E(t)$, it has hysteresis-free, scan rate independent form. That is, $T(E)$ is a state function. To illustrate this statement, two typical cases are worth to be mentioned: (i) In the case when double-layer charging proceeds only, the dc capacitance defined as $j(E)/v$ is independent of v ; (ii) The CVs of reversible redox couples can be transformed to hysteresis-free polarographic-wave shaped curves using semiintegration. In these two cases the scan-rate normalized and semiintegrated currents, respectively, are the scan-rate independent representations of the measured data.

In contrast to the case of the reversible CVs, the CVs of slower redox systems, called quasi-reversible CVs cannot be transformed to a single $T(E)$ function. However, as shown in this paper, by measuring a set of quasi-reversible CVs with different scan rates, two such state functions can be obtained by a simple procedure. One of them characterizes charge transfer kinetics, the other the diffusion. Having derived the relevant equations, the transformation is tested with simulated quasi-reversible CV curves.

2. Theory

Consider a CV measurement of a quasi-reversible redox system [1] with the condition that only the reduced form is present. This species takes part in an n -electron, single-step charge transfer reaction on the electrode. Were the charge transfer not hindered by slow diffusion, the current density would be expressed by the

$$j_{\text{inf}}(E) = k(E)nFc_{\text{red}} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/6600830>

Download Persian Version:

<https://daneshyari.com/article/6600830>

[Daneshyari.com](https://daneshyari.com)