

Monographs in Electrochemistry

Series Editor: F. Scholz

Ángela Molina
Joaquín González

Pulse Voltammetry in Physical Electrochemistry and Electroanalysis

Theory and Applications

 Springer

Ángela Molina • Joaquín González

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Pulse Voltammetry in Physical Electrochemistry and Electroanalysis

Monographs in Electrochemistry

Series Editor: Fritz Scholz, University of Greifswald, Germany

Surprisingly, a large number of important topics in electrochemistry is not covered by up-to-date monographs and series on the market, some topics are even not covered at all. The series Monographs in Electrochemistry fills this gap by publishing indepth monographs written by experienced and distinguished electrochemists, covering both theory and applications. The focus is set on existing as well as emerging methods for researchers, engineers, and practitioners active in the many and often interdisciplinary fields, where electrochemistry plays a key role. These fields will range – among others – from analytical and environmental sciences to sensors, materials sciences and biochemical research.

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Preface of the Editor

Pulse techniques have a long history. Eminent scientists have to be remembered along the pathways of development of modern pulse techniques that are now so frequently used in research and analytical laboratories: Frederick Gardner Cottrell (1877–1948), Mirko Kalousek (1915–1996), Geoffrey Cecil Barker (1915–2000), Robert Allen Osteryoung (1927–2004), to name but a few. Now there are so many different varieties of pulse techniques available that it is difficult to keep an overview and to choose the most appropriate for a certain problem. The authors of this monograph, Ángela Molina and Joaquín González from the Universidad de Murcia, Spain, have undertaken the titanic venture to present a comprehensive and at the same time clearly arranged and systematic survey of pulse techniques. Both authors were best prepared for this task as they have contributed numerous theoretical and experimental studies to this field of electrochemical measuring techniques. The result is the most up-to-date monograph on the theory and application of pulse techniques—a unique book as it has never been written before. I am sure that this monograph will become and remain a first-choice standard work for many years to come.

Greifswald, Germany
March 2015

Fritz Scholz

*Idealization comes first; only then can
description follow*

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Contents

1	Some Fundamental Concepts	1
1.1	Introduction	1
1.2	Outer, Surface, and Inner Potentials	2
1.3	Thermodynamics of Electrochemical Processes	4
1.3.1	Interface Between Two Metals in Contact	6
1.4	Electrochemical Potential of the Electron	6
1.5	Nernst's Equation and Standard Electrode Potentials	8
1.5.1	Formal Electrode Potentials	14
1.6	Electrical Double Layer	15
1.6.1	Models for the Electrical Double Layer	21
1.6.2	Specific Adsorption	25
1.7	Kinetics of the Charge Transfer	27
1.7.1	The Butler–Volmer Model	31
1.7.2	The Marcus–Hush Model	33
1.8	Mass Transport	42
1.8.1	Minimization of the Migration Component	49
1.8.2	Temporal Evolution	50
1.8.3	Convection	50
1.8.4	Mass Transport Coefficient	52
1.9	Three-Electrode Systems. Ohmic Drop, Resistance of the Cell, and RC Time Constant	58
1.10	Pulse Versus Step	63
	References	65
2	Single Pulse Voltammetry: Reversible Electrochemical Reactions	67
2.1	Introduction	67
2.1.1	Reversible Electrode Reaction	69
2.2	Planar Electrodes	69
2.2.1	Concentration Profiles	72

2.2.2	Current–Time Curves (Chronoamperometry) and Current–Potential Curves (Voltammetry)	74
2.2.3	Stoichiometric Coefficients Different From the Unity . . .	79
2.3	Ion Transfer Through Liquid Membranes	81
2.3.1	One-Polarized Interface Systems	82
2.3.2	Two-Polarized Interfaces Systems	84
2.3.3	Electron Transfer at the Liquid/Liquid Interface	90
2.4	Dropping Mercury Electrode (DME)	94
2.4.1	dc Polarography	96
2.4.2	Normal Pulse Polarography (NPP)	99
2.5	Spherical Electrodes	101
2.5.1	Unequal Diffusion Coefficients ($D_O \neq D_R$)	103
2.5.2	Equal Diffusion Coefficients ($D_O = D_R$)	108
2.6	Other Electrodes Geometries	111
2.7	Microelectrodes. Steady-State Voltammetry	120
2.8	Rotating Disc Electrode	123
2.9	Thin Layer Voltammetry	126
	References	129
3	Single Pulse Voltammetry: Non-reversible and Complex Electrochemical Reactions	133
3.1	Introduction	134
3.2	Quasi-reversible and Irreversible Electrochemical Reactions . . .	134
3.2.1	Planar Electrodes	135
3.2.2	Dropping Mercury Electrode	152
3.2.3	Spherical Electrodes and Microelectrodes	154
3.2.4	Microdiscs. Steady-State Voltammetry	163
3.2.5	General Expression for the Stationary Current–Potential Response at Microelectrodes	166
3.2.6	Comparison Between Marcus–Hush and Butler–Volmer Kinetics	167
3.3	Multi-electron Electrochemical Reactions	171
3.3.1	Two-Electron Electrochemical Reactions at Planar Electrodes	173
3.3.2	Two-Electron Electrochemical Reactions at Different Electrode Geometries	180
3.3.3	Non-reversible Two-Electron Electrochemical Reactions	183
3.3.4	General Solution for Multi-electron Electrochemical Reactions	185
3.4	First-Order Chemical Reactions Coupled to Charge Transfer Processes	189
3.4.1	Catalytic Mechanism	193
3.4.2	CE Mechanism	196
3.4.3	EC Mechanism	201
3.4.4	Comparison of the Disturbed Regions by Catalytic, CE, and EC Mechanisms	203

3.4.5	Comparison Between the Current–Potential Curves Corresponding to Catalytic, CE, and EC Mechanisms	205
3.4.6	Determination of Kinetic Parameters	207
3.4.7	Spherical Electrodes	210
3.4.8	ECE Mechanism and Other More Complex Reaction Schemes	216
3.4.9	Catalytic Mechanism at Disc Electrodes	218
3.4.10	Reversible Charge Transfers Preceded and Followed by Several Complexation Reactions in Equilibrium (Ladder Mechanism)	220
	References	225
4	Double Pulse Voltammetries	229
4.1	Introduction	229
4.2	Reversible Electrochemical Reactions	233
4.2.1	Application of a Double Potential Pulse to Electrodes and Microelectrodes of Any Geometry	234
4.2.2	Double Pulse Chronoamperometry and Chronocoulometry	239
4.2.3	Reverse Pulse Voltammetry	247
4.2.4	Differential Double Pulse Voltammetry	252
4.2.5	Differential Normal Double Pulse Voltammetry	260
4.2.6	Additive Differential Double Pulse Voltammetry	260
4.3	Nonreversible Electrochemical Reactions	264
4.3.1	Application of a Double Potential Pulse to Planar and Spherical Electrodes	264
4.3.2	Reverse Pulse Voltammetry	266
4.3.3	Differential Double Pulse Voltammetry	270
4.3.4	Additive Double Differential Pulse Voltammetry	274
4.4	Multi-electron Electrochemical Reactions	278
4.4.1	Application of a Double Potential Pulse to Electrodes of Any Geometry	278
4.4.2	Differential Double Pulse Voltammetry	282
4.4.3	Additive Differential Double Pulse Voltammetry	287
4.5	First-Order Chemical Reactions Coupled to Charge Transfer Processes	291
4.5.1	Catalytic Mechanism at Disc, Spherical, and Planar Electrodes	291
4.5.2	CE and EC Mechanisms at Planar Electrodes	301
4.6	Triple Pulse Voltammetries	311
4.6.1	Reverse Differential Pulse Voltammetry	311
4.6.2	Double Differential Triple Pulse Voltammetry	313
	References	314

5	Multipulse and Sweep Voltammetries I	317
5.1	Introduction	317
5.2	Reversible Electrochemical Reactions	321
5.2.1	Application of a Multipulse Sequence to Electrodes and Microelectrodes of Any Geometry	322
5.2.2	Multipulse Chronoamperometry	325
5.2.3	Cyclic Staircase Voltammetry and Cyclic Voltammetry at Electrodes and Microelectrodes of Any Geometry	328
5.3	Non-reversible Electrochemical Reactions	349
5.3.1	Planar Electrodes	349
5.3.2	Reversibility Criteria	352
5.3.3	Other Electrode Geometries: Microelectrodes and Steady-State Voltammetry	354
5.3.4	Marcus–Hush Kinetics	356
5.4	Advantages of Using Microelectrodes	358
5.4.1	Reduction of Ohmic Drop and Capacitive Effects	359
5.4.2	Neglecting Convection	361
5.4.3	Ultrafast Voltammetry	361
5.4.4	Microelectrode Arrays	362
5.4.5	Nanoelectrodes	364
5.5	Ion Transport Through Liquid Membranes	365
5.5.1	One Polarized Interface	365
5.5.2	Two Polarized Interfaces	367
5.5.3	Micro-ITIES and Asymmetrical Diffusion	369
	References	373
6	Multipulse and Sweep Voltammetries II	375
6.1	Introduction	375
6.2	Multi-electron Electrochemical Reactions	376
6.2.1	Application of a Multipulse Sequence to Electrodes and Microelectrodes of Any Geometry	376
6.3	First-Order Chemical Reactions Coupled with the Charge Transfer	390
6.3.1	Catalytic Mechanism	391
6.3.2	CE and EC Mechanisms	401
6.3.3	ECE Mechanism	407
6.3.4	Reversible Charge Transfers Preceded and Followed by Several Complexation Reactions in Equilibrium at Electrodes of Any Geometry (“Ladder” Mechanism)	410
6.4	Surface-Bound Molecules	415
6.4.1	One-Electron Electrochemical Reactions: Statement of the Problem	416
6.4.2	One-Electron Electrochemical Reactions: Cyclic Voltammetry	433

6.4.3	Two-Electron Electrochemical Reactions	440
6.4.4	Electrocatalytic Processes at Modified Electrodes	448
	References	460
7	Differential Multipulse and Square Wave Voltammetries	463
7.1	Introduction	464
7.2	Reversible Electrochemical Reactions at Electrodes and Microelectrodes of Any Geometry	469
7.2.1	Differential Staircase Voltammetry	469
7.2.2	Differential Multipulse Voltammetry	471
7.2.3	Square Wave Voltammetry	474
7.3	Non-reversible Electrochemical Reactions	485
7.3.1	Differential Multipulse Voltammetry	485
7.3.2	Square Wave Voltammetry	489
7.4	Ion Transport Through Liquid Membranes	499
7.4.1	Differential Multipulse Voltammetry	500
7.4.2	Square Wave Voltammetry	500
7.4.3	Micro-ITIES and Asymmetrical Diffusion	503
7.5	Multi-electron Electrochemical Reactions	507
7.5.1	Reversible Electrochemical Reactions	508
7.5.2	Non-reversible Electrochemical Reactions	520
7.6	First-Order Chemical Reactions Coupled to the Charge Transfer Reaction	522
7.6.1	Catalytic Mechanism	523
7.6.2	CE and EC Mechanisms	528
7.6.3	ECE Mechanism	530
7.6.4	Ladder Mechanism	533
7.7	Surface-Bound Molecules	536
7.7.1	One-Electron Electrochemical Reactions	537
7.7.2	Multi-electron Electrochemical Reactions	557
7.7.3	Electrocatalytic Reactions at Modified Electrodes	563
	References	577
	Appendices	581
	About the Authors	661
	About the Editor	663
	Index	665

Chapter 1

Some Fundamental Concepts

Contents

1.1	Introduction	1
1.2	Outer, Surface, and Inner Potentials	2
1.3	Thermodynamics of Electrochemical Processes	4
1.3.1	Interface Between Two Metals in Contact	6
1.4	Electrochemical Potential of the Electron	6
1.5	Nernst's Equation and Standard Electrode Potentials	8
1.5.1	Formal Electrode Potentials	14
1.6	Electrical Double Layer	15
1.6.1	Models for the Electrical Double Layer	21
1.6.2	Specific Adsorption	25
1.7	Kinetics of the Charge Transfer	27
1.7.1	The Butler–Volmer Model	31
1.7.2	The Marcus–Hush Model	33
1.8	Mass Transport	42
1.8.1	Minimization of the Migration Component	49
1.8.2	Temporal Evolution	50
1.8.3	Convection	50
1.8.4	Mass Transport Coefficient	52
1.9	Three-Electrode Systems. Ohmic Drop, Resistance of the Cell, and RC Time Constant	58
1.10	Pulse Versus Step	63
	References	65

1.1 Introduction

The main purpose of this opening chapter is to provide a brief review of different concepts involved in the study of the current–potential response of electrochemical processes. This is necessary for a better understanding of some aspects of the responses of the different electrochemical techniques analyzed in the following chapters.

The electrostatic aspects of electrochemical systems will be introduced first and the electrochemical potential as a key concept is presented (Sects. 1.2–1.4). The electrochemical equilibrium is discussed and Nernst's equation and standard and formal electrode potentials are introduced (Sect. 1.5). The study of electrochemical interfaces under equilibrium ends with the phenomenological and theoretical treatment of the electrical double layer (Sect. 1.6).

The analysis of the kinetics of the charge transfer is presented in Sect. 1.7 for the Butler–Volmer and Marcus–Hush formalisms, and in the latter, the extension to the Marcus–Hush–Chidsey model and a discussion on the adiabatic character of the charge transfer process are also included. The presence of mass transport and its influence on the current–potential response are discussed in Sect. 1.8.

Finally, some practical questions such as the three-electrode setup, the influence of the ohmic drop, the RC time constant, and a short discussion on the nomenclature of the potential perturbations used in this techniques are addressed in Sects. 1.9 and 1.10.

1.2 Outer, Surface, and Inner Potentials

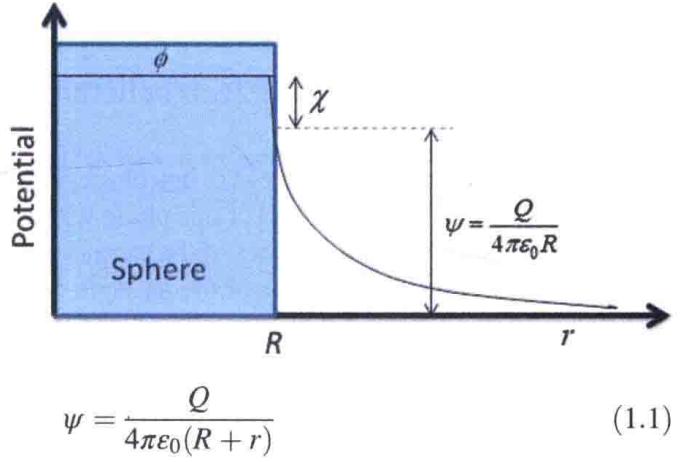
Electrochemistry deals with charged particles that have both electrical and chemical properties. Since electrochemical interfaces are usually referred as electrified interfaces, it is clear that potential differences, charge densities, dipole moments, and electric currents occur at these interfaces. The electrical properties of systems containing charged species are very important for understanding how they behave at interfaces. Therefore, it is important to have a precise definition of the electrostatic potential of a phase [1–6]. Note that what really matters in electrochemical systems is not the value of the potential but its difference at a given interface, although it is illustrative to discuss its main properties.

The potential of a charged species can be divided into different contributions to account for the different arrangements of charges (free charges, oriented dipoles, etc.) that can be found. In order to evaluate these different contributions, a thought experiment can be proposed in which a test charge located at the vacuum at an infinite distance from a given phase is brought inside this phase [3].

The outer or external potential, ψ , of an electrified material phase is defined as the energy required to move this unit test charge from the infinite to a point just outside the phase, with this energy being induced only by the free electrostatic charges, i.e., this potential is purely determined by the charge in the phase and is not influenced by the redistribution of the charge at the surface and the so-called image effects [3, 4, 7]. A distance of about 1 μm fulfills the above requirement and at the same time is not too large to prevent the weakening of the interactions with the charges in the phase. Only the ψ potential and correspondingly $\Delta\psi$ can be experimentally measured [3].

For example, assuming that the phase is an isolated sphere of radius R , the potential experienced by a test positive charge Q is (see Fig. 1.1)

Fig. 1.1 Radial distribution of potential for a metal sphere of radius R carrying a positive charge Q , illustrating the contributions of the outer potential and the surface potential. The inner potential is constant inside the sphere



with ϵ_0 being the vacuum electric permittivity and r the coordinate that defines the movement of the charge.

The surface potential χ of a solid phase is defined as the energy required to move the unit test charge from the infinite toward the anisotropic zone resulting from the surface to the electronic gas which expands beyond the lattice and causes the formation of a dipolar layer although other explanations are possible. During this hypothetical experiment, the charge in the phase turns to zero. Therefore, the potential has nothing to do with the charge of the phase [3, 8].

In the case of a liquid phase, the χ potential is associated with the net preferential orientation of dipoles at the surface. This arrangement is equivalent to a charge separation and a potential difference occurs across the surface dipole layer. The estimation of χ remains unsolved [8].

The inner potential, ϕ , is the sum of the outer and surface potential:

$$\phi = \psi + \chi \quad (1.2)$$

and is related to the energy required to move the unit test charge to a point inside the phase (ϕ is related to the electric field strength E in the interior of the phase by $-\nabla\phi = E$ with ∇ being the gradient operator).

Concerning the potential differences, that corresponding to the outer potentials between two phases α and β is known as the Volta potential difference defined as

$${}^\alpha\Delta^\beta\psi = \psi^\beta - \psi^\alpha \quad (1.3)$$

This is a measurable quantity which is usually called the contact potential difference [4, 6]. The equivalent potential difference for the inner potentials is known as the Galvani potential difference¹,

¹ It may be convenient to regard the Galvani potential difference between two phases in contact as being due to two effects: the orientation of dipoles in the interface between them and the separation of independently mobile charged species across the phase boundary in an analogous way to that discussed for the separation of ϕ into outer and surface potentials [5, 6].

$${}^{\alpha}\Delta^{\beta}\phi = \phi^{\beta} - \phi^{\alpha} \quad (1.4)$$

1.3 Thermodynamics of Electrochemical Processes

The chemical potential of a species “i” in a phase with “m” species is defined as the derivative of the internal energy U of this phase with respect to the number of moles of species “i” (n_i), at constant values of the extensive variables V , S , and the number of moles of the remaining species in the absence of electrical and magnetic fields,

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{V, S, n_{j \neq i}} \quad (1.5)$$

As the condition of constant entropy is difficult to achieve, it is more convenient to fix other variables.

The variation of internal energy can be written in a general way as

$$dU = -PdV + TdS + \sum_i \mu_i dn_i \quad (1.6)$$

and the Gibbs and Helmholtz energies G and A , respectively, are given by

$$G = U + PV - TS \quad (1.7)$$

$$A = U - TS \quad (1.8)$$

By deriving Eqs. (1.7) and (1.8), and inserting into the result that corresponding to dU (Eq. (1.6)), the expression of the chemical potential given by Eq. (1.5) can be also written as

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}} \quad (1.9)$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (1.10)$$

The chemical potential is defined as the change of energy of a phase when an additional mol of particles of species i is introduced at fixed V and S , T and V , or T and P . The most usual definition of the chemical potential is the necessary work to introduce one mole of species i from the infinite to a phase at fixed T and P (i.e., as given in Eq. (1.10)).