ELECTROANALYTICAL CHEMISTRY

Edited by
ALLEN J. BARD

VOLUME 14

ELECTROANALYTICAL CHEMISTRY

A SERIES OF ADVANCES

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Introduction to the Series

This series is designed to provide authoritative reviews in the field of modern electroanalytical chemistry defined in its broadest sense. Coverage will be comprehensive and critical. Enough space will be devoted to each chapter of each volume so that derivations of fundamental equations, detailed descriptions of apparatus and techniques, and complete discussions of important articles can be provided, so that the chapters may be useful without repeated reference to the periodical literature. Chapters will vary in length and subject area. Some will be reviews of recent developments and applications of well-established techniques, whereas others will contain discussion of the background and problems in areas still being investigated extensively and in which many statements may still be tentative. Finally, chapters on techniques generally outside the scope of electroanalytical chemistry, but which can be applied fruitfully to electrochemical problems, will be included.

Electroanalytical chemists and others are concerned not only with the application of new and classical techniques to analytical problems, but also with the fundamental theoretical principles upon which these techniques are based. Electroanalytical techniques are proving useful in such diverse fields as electro-organic synthesis, fuel cell studies, and radical ion formation, as well as with such problems as the kinetics and mechanisms of electrode reactions, and the effects of electrode surface phenomena, adsorption, and the electrical double layer on electrode reactions.

It is hoped that the series will prove useful to the specialist and nonspecialist alike—that it will provide a background and a starting point for graduate students undertaking research in the areas mentioned, and that it will also prove valuable to practicing analytical chemists interested in learning about and applying electroanalytical techniques. Furthermore, electrochemists and industrial chemists

with problems of electrosynthesis, electroplating, corrosion, and fuel cells, as well as other chemists wishing to apply electrochemical techniques to chemical problems, may find useful material in these volumes.

A.J.B.

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Precision in Linear Sweep and Cyclic Voltammetry

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I. INTRODUCTION

The purpose of this chapter is to discuss some recent developments in cyclic voltammetry (CV) and linear sweep voltammetry (LSV). At the outset, I wish to stress that the work described does not involve a radically new approach to these subjects, but rather a new *emphasis* which affects the manner in which experiments are carried out and the way in which the data are treated. The attempts to improve the precision of the measurements are particularly noteworthy. The level of precision in the measurement of electrode peak potentials has been improved by nearly an order of magnitude, while errors inherent in the determination of peak current ratios during CV have been minimized by derivative techniques. It has been shown that rate laws of homogeneous reactions following charge transfer can be derived directly from experimental CV and LSV data without the assumption of theoretical models. This is particularly useful in cases where experimental data are not ideal and do not provide good comparisons with theoretical working curves.

A vast amount of work dealing with CV and LSV has been published. It is beyond the scope of this chapter to review this material. In the past few years there have been two detailed and excellent accounts of these topics published with somewhat differing viewpoints. Bard and Faulkner [25] develop electrochemical methods from the beginning to an advanced stage, including practical examples. MacDonald [36] concentrates on the theoretical aspects and calculational methods of the transient techniques. Pertinent literature references are thoroughly covered in these monographs.

II. ELECTRODE MECHANISM ANALYSIS

In this chapter "electrode mechanism" refers to the sequence of reactions following charge transfer of intermediates generated in Nernstian electron transfer processes. The discussion is concerned only with reactions taking place in solution; surface processes are not considered.

A. Direct vs. Indirect Methods

By definition, we consider direct kinetic methods to be those which involve the monitoring of the response of the intermediate undergoing chemical reactions. Indirect methods are those which monitor the effect of the chemical reactions on the response of the substrate. The discussion is concerned primarily with LSV and CV. Of these, LSV is an indirect and CV is a direct kinetic method. Other combinations of the two types of methods are as follows:

Indirect	Direct
Rotating disk electrode voltammetry	Rotating ring disk electrode voltammetry
Chronoamperometry	Double-potential-step chronoamperometry
Chronopotentiometry	Current reversal chronopotentiometry