

1 Introduction

Electrochemistry is an extremely interdisciplinary area of science closely related to chemistry, physics, materials science, biology, surface science and a host of other fields. It is basically devoted to investigations of structures and dynamics as being present at interfaces between phases containing different types of mobile charged particles. Thus the process of electrochemical production of chlorine proceeding at the surface of a metal electrode in contact with a halide-containing solution in chlorine-alkali electrolysis is a typical case of electrochemistry at work. In the electrode the mobile charges are electrons, which are withdrawn from the chloride anions that are the mobile charged species in the solution phase. The interface established between molten iron and the fairly complicated mixture of molten metal oxides floating on top of the molten metal is another example. The stimulation of nerves and the propagation of information along nerves is another, totally different case. One more different case is the delamination of an organic coating applied to a metal surface for corrosion protection that occurs because of processes occurring at the metal-coating interface in the presence of a thin solution film on top of the coating containing small concentrations of electrolyte salts. In all of the examples just mentioned charged particles and large electric fields at interfaces play a pivotal role in establishing the structure at the interface and in controlling the various processes occurring at the interface. These examples share an additional feature that may possibly complicate their investigation: All interfaces are “buried” between two condensed phases (liquid or solid). Electrochemical investigations have focused in recent decades on elucidating their static and dynamic features exactly. The breadth of the few listed examples illustrates the need for intense research. Beyond these aspects of interfacial electrochemistry, the processes and structures within a condensed phase containing ions far away from the interface with their particular properties are the other main topics of electrochemistry. They are related to ionic conduction, thermodynamics of perfect (ideal) and real phases and other topics that are of only peripheral interest within the scope of this book. Initial investigations of electrochemical interfaces were limited to the measurements of electrical and chemical quantities, e.g. current, voltage, potential, charge or concentration. Kinetics could be elucidated by performing these measurements as a function of time, concentration and temperature. Unfortunately the obtained results provided in most cases only a very rough and macroscopic picture. A complete understanding, in particular at the microscopic level, was impossible or only highly speculative. With the

increasing importance and breadth of the application of electrochemistry in industry, technology and daily life, this has become a considerable obstacle. Optimization of a given system or process and the understanding of the failure of a product with electrochemical features is possible only based on a deeper understanding of the electrochemical interface.

The advent of a broad variety of methods in vacuum physics, surface and materials science and analytical chemistry has provided a rich zoo of methods that have been converted for use in experimental electrochemistry. In contrast to the experimental methods briefly touched upon before, these methods are summarized as “non-traditional methods”.

The overwhelming abundance of available methods is a tremendous possibility and a considerable seduction. Reasonable use of available methods and selection of the most suitable ones is possible only based on at least a minimum knowledge of the available methods, their strengths and weaknesses and their known pitfalls. So far the researcher has to consult either the original literature, including numerous more or less strongly focused reviews, or quite a few books that provide overviews of some subfamilies of the large number of available methods. The present book attempts to provide a broad overview delving into the depth of a certain method only as far as necessary to provide an initial understanding. It attempts to include all known methods of investigation applied to electrochemical interfaces that have arrived at a stage where a useful application has become visible to a broader audience.

In the following chapters and sections this will be done in a way that will hopefully be useful for the researcher looking for a method for his particular problem and for the graduate student looking for possible methods to treat the task of his masters thesis. In the second chapter, the structure and dynamics of electrochemical interfaces will be reviewed briefly. The term “interphase” will be introduced, stressing the fact that the topmost layers or regions of both phases that are in contact at the interface are different from layers and regions within the bulk of the phases. The third chapter pays a closer look at the possibilities of classical electrochemical methods and stresses the limitations beyond which traditional electrochemical methods provide only the basis for speculative interpretation of experimental data.

In Chap. 4, spectroscopic and surface analytical methods that form the bulk of this book are treated in the form of a general overview. This chapter will be of interest for a reader with an already established background in traditional electrochemistry who is looking for a general introduction. Chapter 5 provides the complete picture of spectroscopic methods. Chapters 6 and 7 treat X-ray and surface topographic methods. A brief introduction explains the way methods are assigned to various families. Descriptions of the available methods as known to the author are provided together with instructive examples of their applications. The structure of a description always follows the same scheme. The fundamentals are presented briefly. The electrochemical system properties that can be investigated with the method are indicated. A description of the experimental setup is provided. Some examples serve as illustration. References are provided especially for methods and experimental de-

tails that cannot be treated exhaustively within the limited scope of this book. No attempt is made to provide a complete listing of all reported applications of a given technique.

A generous list of acronyms is provided, giving the reader access to fast explanations of the myriad of examples of the modern letter soup omnipresent in scientific papers. The subject index will serve as a fast access lane especially for those readers searching for information about a particular method.



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