Arvydas Survila

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Electrochemistry of Metal Complexes

Applications from Electroplating to Oxide Layer Formation
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Preface

Chemical processes involving metal complexes can be found at every step, from the transformations observed in nature and ending with the various chemical industries, purposefully carried out by man. Among the latter are prominent processes occurring at the interface metal/solution, the end result of which is a production of electric energy or production of various products of electrolysis, including metallic coatings having a different purpose.

Qualitative anticorrosive, decorative, abrasion-resistant, and heat-resistant coatings are usually obtained by the electrolysis of solutions containing coordination compounds (complexes) of metals. Electrochemical processes involving these compounds are rather complicated because they proceed through several different stages, such as the mass transfer of chemically interacting particles, adsorption, charge transfer, formation of new phases, and so on.

Various problems of the electrochemistry of these systems have frequently been discussed in the literature including my book: A. Survila, Electrode Processes in Systems of Labile Complexes of Metals (Mokslas, Vilnius 1989), published some time ago. Since then, a long time has passed and there has been progress in the field of theory and practice, in the field that deserves comprehension and generalization. In this regard, there was an interest to write a book in which all the major stages of electrochemical processes (mass transport, adsorption, charge transfer) are sequentially covered, putting special emphasis on their deep interrelation. I decided on this difficult task, using data published at different times in the literature, as well as theoretical and experimental material accumulated in the last half-century. In addition, it seemed appropriate to present in this book not only basic questions of electrochemistry of metal complexes including the actual plating problems, but also some other phenomena that would be possible to be classified as “related”. I hope that spontaneous formation of semiconducting oxide layers, appearance of current oscillations, specifics of hydrogen evolution could also be of interest to the reader.

The material presented in this book is divided into 11 chapters. A systematic analysis of electrochemical processes involving metal complexes starts with general considerations on equilibria in solutions (Chapter 1). Their main equilibrium properties are considered and general principles of quantitative description of their composition are presented. Acquaintance with the equilibrium properties of
complex systems continues in Chapter 2, which analyzes the processes occurring at the interface metal/solution and discusses the electrodes of the first and second kinds. The principles of their quantitative descriptions are presented together with selected experimental data. Along with the known points, the reader will also find a description of other, less known self-extinguishing characteristics of these systems. This part of book is intended to provide background information, sufficient for an intelligible understanding of the material that is developed in next chapters.

Next chapters acquaint readers with the theory and common experimental practice for studying electrochemical reactions of metal complexes. Regularities of mass transport of chemically interacting particles considered in Chapter 3 serve for determining the surface concentrations of complexes and ligands. Furthermore, these data make it possible to reveal the peculiarities of electrochemical processes (Chapter 4) and form the basis for quantitative modeling of electrochemical processes (Chapter 5) and determining their mechanism (Chapter 6).

Theoretical developments are widely used in experimental investigation of real electrochemical systems (Chapters 8 and 9). The core part of the book deals with all important aspects of electroplating, including a systematic discussion of codeposition of metals and formation of alloys. It also discusses such related subjects as oxide layer formation (Chapter 10) and hydrogen evolution as a side reaction (Chapter 11).

The material presented in this book are designed for a wide range of readers. A major part of the material included in this book was presented at Vilnius University for senior students who have completed introductory courses in chemistry of coordination compounds and electrochemistry, though the first two chapters are easy comprehensible even for younger students. Problems regarding the quantitative description of electrochemical processes and the determination of their mechanism differ in complexity. Some of them are aimed at senior graduate or postgraduate students; others suggest a higher level of competence and, it is hoped will also be of interest to professional electrochemists.

Materials relating to the processes occurring in real systems may be useful for people working in engineering or manufacturing. The same can be said about Chapter 10. Electrochemical mechanisms and the role of ligand in formation of light-sensitive oxide layers may be of interest to researchers who have less contact with the electrochemistry.

In the book, much space is allotted to theoretical and experimental research performed by the author at the Institute of Chemistry (at present, Center of Physical Sciences and Technology, Vilnius, Lithuania) in collaboration with a capital research team. I wish to acknowledge a valuable contribution of my coauthors, whose names appear in the literature references. Two persons I would like to mention particularly. One of them is a nice experimenter Stasė Kanapeckaitė, with whom I had a pleasure to work with successfully for several decades. Another is
my wife Audronė Survilienė, who not only carried out a number of important experiments but also created the conditions for the successful work on this book.

Vilnius, 2015

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Symbols and Abbreviations

Subscripts

a anodic
b bulk
c cathodic
c_t charge transfer
d diffusion
dl double layer
eq equilibrium
f_b flat band
F Faradaic
H proton donors and acceptors
i nversion
l_m limiting
L ligand
M metal
N Nernstian
O oxidant
o_c open circuit
p peak
p_o_l polarization
r reaction
R reductant
s surface
Ω ohmic
1/2 half-wave