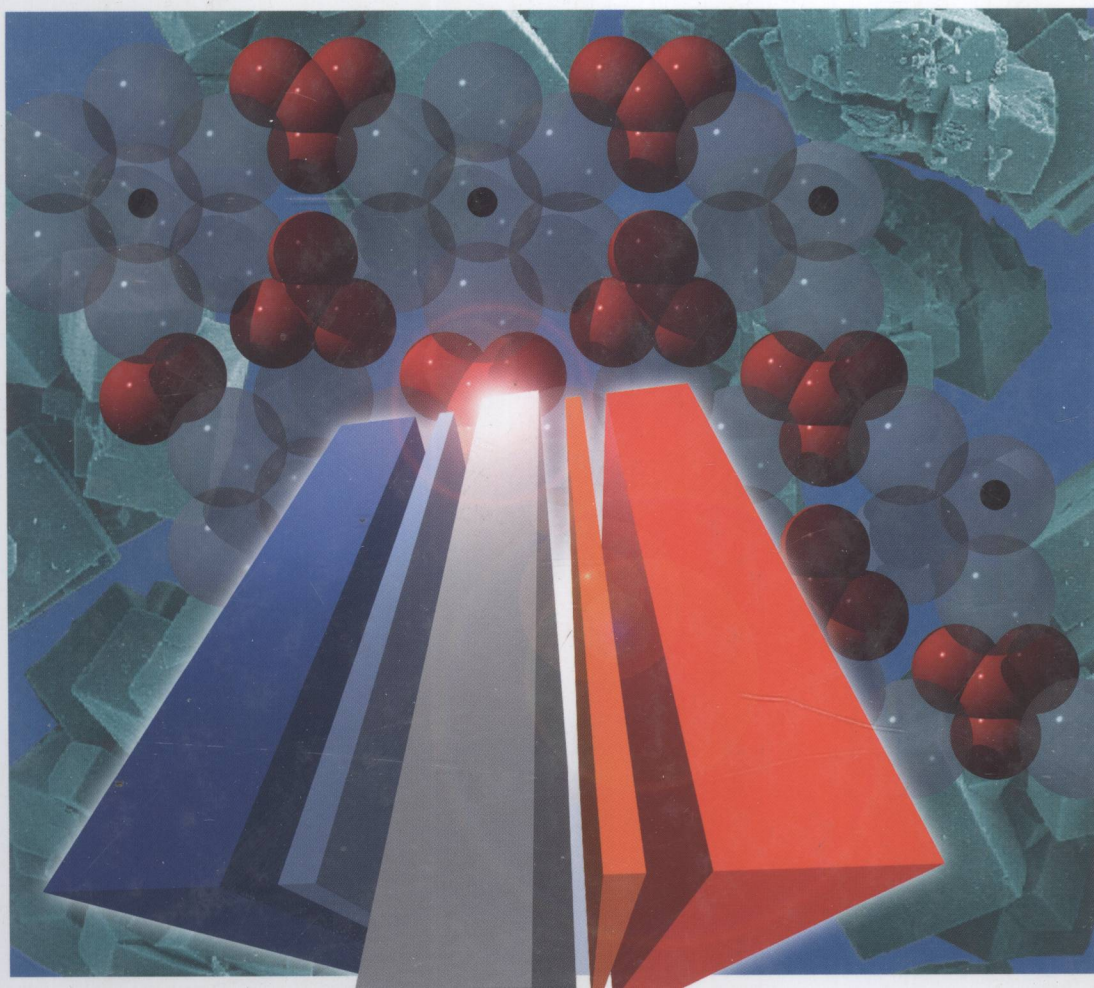


Edited by Vladislav V. Kharton

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Fundamentals, Materials and their Applications



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Edited by

Vladislav V. Kharton



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Preface

Vladislav V. Kharton

Solid-state electrochemistry is an important and rapidly developing scientific field that integrates many aspects of classical electrochemical science and engineering, materials science, solid-state chemistry and physics, heterogeneous catalysis, and other areas of physical chemistry. This field comprises – but is not limited to – the electrochemistry of solid materials, the thermodynamics and kinetics of electrochemical reactions involving at least one solid phase, and also the transport of ions and electrons in solids and interactions between solid, liquid and/or gaseous phases, whenever these processes are essentially determined by the properties of solids and are relevant to the electrochemical reactions. The range of applications includes many types of batteries and fuel cells, a variety of sensors and analytical appliances, electrochemical pumps and compressors, ceramic membranes with ionic or mixed ionic-electronic conductivity, solid-state electrolyzers and electrocatalytic reactors, the synthesis of new materials with improved properties and corrosion protection, supercapacitors, and electrochromic and memory devices.

The first fundamental discoveries, which today are considered the foundation of solid-state electrochemistry, were made during the nineteenth century and the first half of the twentieth century by M. Faraday, E. Warburg, W. Nernst, C. Tubandt, W. Schottky, C. Wagner, and other famous scientists. Such investigations provided the background for the rapid progress achieved both in our understanding of solid-state electrochemical processes, and in the applied developments that were made during the latter part of the twentieth century. As the scope of this volume is limited, and so cannot provide an exhaustive analysis of the historical aspects and classical concepts, those readers interested in such information are referred to a range of well-known books [1–11]. It should be mentioned that, similar to any other scientific area, the continuous progress in solid-state electrochemistry leads both to new horizons and to new challenges. In particular, increasing demands for higher-performance electrochemical cells leads to a need to develop novel experimental and theoretical approaches for the nanoscale optimization of the cell materials and interfaces, for the analysis of highly nonideal systems, and for overcoming the numerous gaps in our knowledge, which became possible only due to recent achievements in the related areas of science and technology. Moreover, the increasing amount and diversity of available scientific information acquired during the past few decades

has raised the importance of systematization, the unification of terminology, and the standardization of experimental and simulation techniques.

The aim of this Handbook is to combine the fundamental information and to provide a brief overview of recent advances in solid-state electrochemistry, with a primary emphasis on methodological aspects, novel materials, factors governing the performance of electrochemical cells, and their practical applications. The main focus is, therefore, centered on specialists working in this scientific field and in closely related areas, except for a number of chapters which present also the basic formulae and relevant definitions for those readers who are less familiar with theory and research methods in solid-state electrochemistry. Since it has been impossible to cover in total the rich diversity of electrochemical phenomena, techniques and appliances, priority has been given to recent developments and research trends. Those readers seeking more detailed information on specific aspects and applications are addressed to the list of reference material below, which includes both interdisciplinary and specialized books [8–20].

The first volume of this Handbook contains brief reviews dealing with the general methodology of solid-state electrochemistry, with the major groups of solid electrolytes and mixed ionic-electronic conductors, and with selected applications for electrochemical cells. Attention is drawn in particular to the nanostructured solids, superionics, polymer and hybrid materials, insertion electrodes, electroanalysis and sensors. Further applications, and the variety of interfacial processes in solid-state electrochemical cells, will be examined in the second volume.

The chapters of the Handbook are written by leading experts in solid-state electrochemistry from Australia, China, France, Germany, Israel, Japan, Korea, Portugal, Russia, the United Kingdom, and the United States of America. Sadly, one of the authors of Chapter 3, Professor Alexander N. Petrov, died during the finalization stages of the Handbook. His professionalism and love of science will be well remembered by all of his colleagues, and the intellectual contributions made by Professor Petrov will continue to live on in the form of the inspiration that he has provided to his students, coworkers and, hopefully, the readers of this book.

References

- Schottky, W., Uhlich, H. and Wagner, C. (1929) *Thermodynamik*, Springer, Berlin.
- Kröger, F.A. (1964) *The Chemistry of Imperfect Crystals*, North-Holland, Amsterdam.
- Delahay, P. and Tobias, C.W. (eds) (1966) *Advances in Electrochemistry and Electrochemical Engineering*, Wiley-Interscience, New York.
- Kofstad, P. (1972) *Nonstoichiometry, Diffusion and Electrical Conductivity of Binary Metal Oxides*, Wiley-Interscience, New York.
- Geller, S. (ed.) (1977) *Solid Electrolytes*, Springer, Berlin, Heidelberg, New York.
- Rickert, H. (1982) *Electrochemistry of Solids. An Introduction*, Springer, Berlin, Heidelberg, New York.
- Chebodin, V.N. (1989) *Chemical Diffusion in Solids*, Nauka, Moscow.
- Bruce, P.G. (ed.) (1995) *Solid State Electrochemistry*, Cambridge University Press, Cambridge.
- Gellings, P.J. and Bouwmeester, H.J.M. (eds) (1997) *Handbook of Solid State Electrochemistry*, CRC Press, Boca Raton.

- 10 Allnatt, A.R. and Lidiard, A.B. (2003) *Atomic Transport in Solids*, Cambridge University Press, Cambridge.
- 11 Bard, A.J., Inzelt, G. and Scholz, F. (eds) (2008) *Electrochemical Dictionary*, Springer, Heidelberg, Berlin.
- 12 West, A.R. (1984) *Solid State Chemistry and its Applications*, John Wiley & Sons, Chichester.
- 13 Goto, K.S. (1988) *Solid State Electrochemistry and Its Applications to Sensors and Electronic Devices*, Elsevier, Amsterdam.
- 14 Schmalzried, H. (1995) *Chemical Kinetics of Solids*, VCH, Weinheim.
- 15 Munshi, M.Z.A. (ed.) (1995) *Handbook of Solid State Batteries and Capacitors*, World Scientific, Singapore.
- 16 Vayenas, C.G., Bebelis, S., Pliangos, C., Brosda, S. and Tsiplakides, D. (2001) *Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion, and Metal-Support Interaction*, Kluwer/Plenum, New York.
- 17 Hoogers, G. (ed.) (2003) *Fuel Cell Technology Handbook*, CRC Press, Boca Raton.
- 18 Wieckowski, A., Savinova, E.R. and Vayenas, C.G.,(eds) (2003) *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, Marcel Dekker, New York.
- 19 Monk, P.M.S., Mortimer, R.J. and Rosseinsky, D.R. (2007) *Electrochromism and Electrochromic Devices*, 2nd edition, Cambridge University Press, Cambridge.
- 20 Zhuiykov, S. (2007) *Electrochemistry of Zirconia Gas Sensors*, CRC Press, Boca Raton.

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