

11

Part A

**ELECTRODES OF  
CONDUCTIVE  
METALLIC OXIDES**

Edited by **S. Trasatti**

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studies in physical and theoretical chemistry 11

# ELECTRODES OF CONDUCTIVE METALLIC OXIDES

## Part A

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# **ELECTRODES OF CONDUCTIVE METALLIC OXIDES**

**Part A**

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## PREFACE

*"I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the seashore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me."*

Isaac Newton

The discovery by Beer in the second half of the sixties that the performances of anodes made of thermally prepared noble metal oxides were better than those of noble metals provoked something of a technological revolution in the large electrolytic industry. This was not recorded by the open scientific literature. The first concrete fundamental investigation on the topic appeared in the early seventies when such electrodes had already accumulated a long industrial use.

The technological impact of the so-called "*Dimensionally Stable Anodes*" (DSA) based on mixed oxides whose active component is mainly  $\text{RuO}_2$  has been decisive. Further developments are expected and pursued actively. Properties whose improvement is sought for are essentially electrical conduction, chemical stability and electrocatalytic activity.

Since the early work, an ever increasing number of fundamental studies has been published. Research work has been extended to a larger and larger number of single and mixed oxides. A further step consists in mixing three or more components. However, the large amount of available data has not yet been adequately assimilated. The first great technological jump is being followed with a somewhat larger induction time by the step of comprehension of all of the aspects of the phenomenon. Experimental attempts very often rest on an empirical basis. Many of them are simply dictated by the need of circumventing existing patents. A predictive basis for the design and optimization of catalysts can hardly be found behind most of the work.

There is still no publication trying to organize the matter adequately. A gap may still be recognized between the amount of practical applications of oxide electrodes and the knowledge of their fundamental properties. Electrochemical studies have not always been adequately paralleled by the investigation of physical and chemical properties belonging to the field of surface and solid state chemistry

and physics. It is now strikingly evident that the study of oxide electrodes calls for experimental and theoretical approaches which go beyond the traditional field of electrochemistry.

This book is designed to cover the above gaps. It provides a general unifying introduction to the matter together with an up-to-date presentation of the state of the art both in research and technology. The main purpose is to trace a conceptual route linking the physicochemical properties of metallic oxides with their electrochemical performances. In the future, it is hoped that this work will constitute a useful reference and starting point for further developments.

The work was originally envisaged as a single book of twelve chapters, the first four being devoted to topics which are a necessary tool for modern electrochemists to approach properly and fruitfully the field of oxide electrodes. Reasons for splitting the book into two volumes, Part A and Part B, respectively, were twofold: first, the large amount of material to treat; second, the difficulty of collecting all the chapters at one and the same time. The latter reason is extremely relevant in a rapidly developing field like this. Being up-to-date cannot be left out of consideration without seriously limiting the scope itself of this work.

The splitting of the book into two parts has left unaltered the logical sequence previously planned for the strictly electrochemical chapters. Part A deals with structural and thermodynamic properties; Part B is mainly devoted to kinetic and electrocatalytic aspects. However, electrocatalytic reactions still not tractable on a general basis, and some unpublished material on electrocatalysis of oxygen and chlorine only available to the authors of the various chapters have been included in Part A. The four introductory chapters have been equally divided between the two parts to balance the material.

The first chapter of the present Part A is devoted to the description of the electronic structure of oxides. It may still be surprising that oxides, usually regarded as insulators or semiconductors, are in some not uncommon cases better conductors than a number of metals. The chapter shows why this may happen and offers some mathematical tools for band structure calculations.

The second chapter gives an introductory account of chemisorption and catalysis in the gas phase. It is well known that electrocatalysis is still largely dependent on concepts and treatments from the field of heterogeneous catalysis. The chapter provides a general introduction to the matter with examples and applications in the specific field of oxides. It shows that even in heterogeneous catalysis the use of correlations still dominates the purely theoretical approaches, which testifies to the complexity of the topic.

The importance of the study of electrolytically grown oxides to understand better the behaviour of thermally prepared materials is underlined in the third chapter. The mechanism of oxygen evolution on these oxides is also discussed, being the basis from which the analogous discussion for thermally prepared oxides starts.



Chapters 4 through 7 present the state of the art of the research work on the commonest oxides presently used in electrochemistry. These have been separated according to their crystal structure, which is the most immediate way of classifying these materials. However, chapter 4 is devoted to  $\text{PbO}_2$  alone. This material provides a general, clear example of the complexity of the transformations taking place in an oxide when the potential is changed. The other chapters are devoted to spinel-, perovskite-, and rutile-type oxides. They provide a general introduction by describing the more relevant physicochemical properties and discussing the basic electrochemical properties.  $\text{MnO}_2$  has not been treated separately, in spite of its large use both in research and in technology, for two reasons: first, because of the vast literature already covering the matter; second, because the use as an anode, more relevant here, is still limited compared to other oxides yet treated in a group.

The Editor is indebted to his colleagues and friends Roger Parsons and Gaetano Lodi: the former for reading and commenting on some of the chapters, the latter for his invaluable technical assistance in the preparation of the "camera-ready copy".

*Milan, Italy*  
*April 1980*

Sergio Trasatti



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## CHAPTER 1

# ELECTRONIC BAND STRUCTURE OF OXIDES WITH METALLIC OR SEMICONDUCTING CHARACTERISTICS

*J. M. Honig*

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## I. INTRODUCTION

### A. General Comments

Oxides which are chemically inert and which exhibit metallic characteristics have been found useful in many technological applications. This has brought about an upsurge of interest in their distinctive electrical properties. In this chapter we examine various theoretical methods for the characterization of these materials with respect to their band structures.

Oxides as a group may be placed in three broad categories: insulators (or semiconductors), metals, and materials undergoing metal-insulator transitions. Traditionally, metal oxides have been viewed as being insulators. It thus comes as a surprise to many scientists to learn of the growing catalog of such materials which display metallic characteristics. Included in this grouping is a special category of oxides that undergo metal-insulator transitions on heating or cooling. The class of insulators may itself be subdivided into those for which the carriers responsible for charge transport (electrons or holes) are largely localized, and those that are insulating because a large energy gap  $E_g$  - which greatly exceeds the thermal energy  $kT$  of carriers in the lattice at temperature  $T$  - separates nearly filled from nearly empty band states. Carriers which are thermally available in this latter subgroup are itinerant.

While materials with localized carriers are of great interest and present many challenges to the theoretician they do not exhibit metallic properties and therefore will not be considered further. Itinerant semiconductors as such would normally also fall outside the scope of the present review, were it not for the fact that these materials can frequently be doped with altrivalent impurity ions, rendered nonstoichiometric, or alloyed with other oxides. Any of these procedures injects charge carriers into the bands; depending on the extent of doping the material can then be converted into a degenerate semiconductor or a reasonably good metal: this class of substances finds applications from solar energy conversion devices to electrode materials. The metallic oxides may also be divided into two subgroups: those characterized by an incomplete filling of the band or bands and those where band overlap occurs. Materials in this latter group are sometimes termed semimetals. Oxides in either of these groupings are very similar in properties to the more



## INTRODUCTION

conventional metals such as Cu, Fe, or Au. Finally, the materials which undergo metal-insulator transitions may be grouped into many subcategories according to the mechanisms which are thought to be responsible for these transitions; one example is described in detail in sec. VI.E.

In many cases the distribution between the various categories is blurred: it may not be easy to decide whether a material is to be characterized by extremely narrow bands or by a localized energy scheme. Likewise, the distinction between metals characterized by an incomplete filling of bands or by band overlap is vague. Nevertheless, the above grouping forms a very convenient zero order classification scheme.

It is the aim of this paper to provide a reasonably self-contained and systematic discussion of topics so that a reader can understand how oxides can exhibit such vastly different physical characteristics. Also, background information is provided so that one can make predictions concerning the electrical characteristics which a given oxide is likely to display.

The plan of the article is as follows: after some introductory material on one-dimensional materials a qualitative scheme is developed for rationalizing a large body of experimental observation pertaining to electrical properties of oxides. The theoretical discussion then is enlarged to include three-dimensional materials. Based on this, relatively elementary quantitative theories of band structures are developed. The review is terminated with a description of rather sophisticated band structure calculations, and with a short discussion of one mechanisms of metal-insulator transitions.

This article will have served its purpose if it stimulates the reader to engage in a further perusal of the literature on this subject. Several representative reviews pertaining to metallic oxides are provided in Refs. 1 to 10.

### B. The Particle-in-a-Box Model

Before discussing metallic oxides as a group it is desirable to review briefly some of the elementary models used to characterize lattices with metallic properties. As a rock bottom approximation one employs the well-known particle-in-a-box model to simulate the solid under study; the electrons are subjected to a potential well of constant magnitude acting over a definite crystal volume, outside of which the electronic potential energy is extremely large. The energy of the particles is quantized, but for a crystal volume of macroscopic (*i.e.* laboratory) dimensions successive energy levels are so closely spaced as to form almost a continuum. The individual levels are filled in accordance with the Pauli exclusion principle; the cutoff energy which at the absolute zero of temperature separates the filled from the unfilled states is known as the *Fermi level* (Fermi energy),  $E_F$ . All

electrons have access to the entire volume of the crystal. However, for normal metals,  $E_F^*$  greatly exceeds the average thermal energy  $\frac{1}{2}kT$  for a particle with one degree of freedom; hence, one is led to the Sommerfeld model, in which only electrons within an energy range  $kT$  of  $E_F$  provide a net response to applied fields.

Clearly such a model is too simplistic to be useful in the description of metallic oxides; for, the very existence of constituent lattice atoms is not recognized in specifying the potential energy.

### C. The Kronig-Penney Model

A significant improvement on the above model is achieved by use of the Kronig-Penney procedure. Here the presence of atoms is simulated by a periodic array of square well potentials as depicted in Fig. 1. One must distinguish between the set of 'valleys' of potential energy  $V = 0$  representing atomic sites and the set of 'hills', associated with the potential energy  $V = V_0$ , separating the atomic sites. One must then solve the Schrödinger equation in one dimension

$$\left\{ -\left(\frac{\hbar^2 \nabla^2}{2m}\right) + V - E \right\} \psi(x) = 0 \quad (1)$$

where  $V = 0$  or  $V = V_0$  depending on the region of space under study.

To solve eqn. (1) it is expedient, in conformity with a theorem originally developed by Floquet, to switch from the dependent variable  $\psi(x)$  to a new variable  $u(x)$  by writing

$$\psi(x) = \exp(ikx)u_k(x) \quad (2)$$

with the additional periodicity requirement

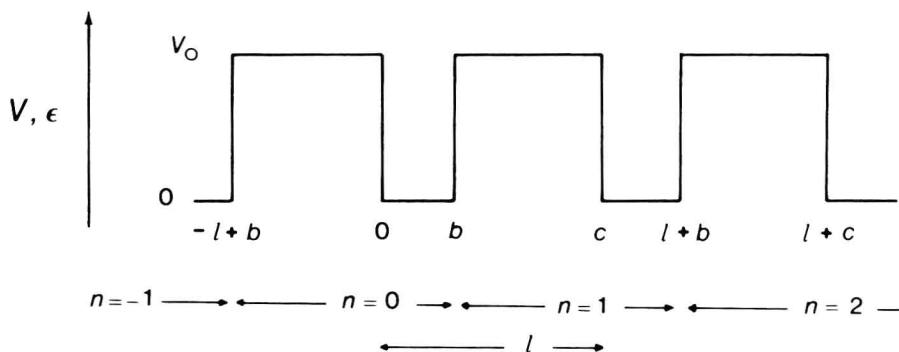


Fig. 1 - One dimensional Kronig-Penney model.

\* Note that in some of the figures the symbol  $\epsilon$  is used instead of  $E$ .