Preface

This book focuses on nanotechnology in electrocatalysis for energy applications. In particular it covers nanostructured electrocatalysts for low temperature fuel cells, low temperature electrolyzers, and electrochemical valorization of carbon dioxide.

In recent years a variety of papers have been published on this subject. Nevertheless, the availability of introductory monographs on such a hot topic is still limited.

Researchers and professionals new to this field often find it difficult to navigate through the huge amount of information being constantly produced in such a quickly growing area. For this reason we have tried to design a book whose function is to provide an introduction to the basic principles of electrocatalysis, together with a review of the main classes of materials and electrode architectures. We feel that this approach has the potential to illustrate the basic ideas behind material design, providing also an introductory sketch of the current research focuses. The book is conceived to be as self-contained as possible. Here and there, especially in the chapters concerning basic thermodynamic and kinetic principles, we advise the reader to refer to the many excellent textbooks that already cover these areas. We hope we have succeeded in making this book readable enough to allow a graduate in technical and scientific disciplines with a fair background in chemistry (i.e. physicists, engineers, chemists, electrochemists, etc.) to understand the basic concepts. A reader with such a background will experience a gentle introduction allowing him to grasp the main design criteria driving the development of new nanomaterials for electrocatalysis. We also hope that the material presented in the book will help the reader to seek more specialized literature, developing his or her own opinion about the pros and cons of the very many existing approaches (at times, a nontrivial task).

The subject has been limited to low temperature electrocatalysis (below 120 °C). We are conscious that this is a limit. But on the other hand, extension to high temperature systems would have required much more space and the illustration of a variety of complex principles, something we believe does not match the original objectives we had for this book.

Discussion focuses on the three main fields where nanostructured and molecular electrocatalysts play a major role: (i) polymer electrolyte membrane fuel cells, (ii) electrolytic hydrogen production, and (iii) CO₂ electroreduction.
The book consists of three parts. After a short introduction (Chap. 1) that reports the general framework and outlines the concept of the book. Part I, entitled *Fundamentals*, then begins. This is aimed at giving an introduction to the basic concepts of electrocatalysis (Chap. 2), also describing the main devices where nanomaterials are exploited (Chap. 3). The text has been organized in such a way that no complex derivations or lengthy descriptions are given. Only the major formulas and concepts are reported in a simple fashion, to help the reader to understand the philosophy behind electrocatalytic material development. This part closes with a discussion of the factors affecting the design of electrocatalysts (Chap. 4), describing the main issues and also stressing the constraints which have to be necessarily accounted for. After such a discussion the role of nanotechnology in addressing the targets for effective electrocatalyst development is considered.

Building upon sound foundations, the description of the various materials begins. Each chapter regarding materials begins with a key concepts paragraph, giving the essential background that lies behind the development of research in each area.

Part II, entitled *Support Materials*, is devoted to catalyst support materials. The part starts (Chap. 5) with a discussion of carbon blacks, the ubiquitous porous carbons widespread in commercial electrocatalyst technology. Then carbon nanomaterials are reviewed, with a special emphasis on the “rising stars,” such as carbon nanotubes and graphene. Chapter 6 deals with other support materials. Titania nanotubes and other conducting oxides are considered. These are especially important for fuel cells fed with liquid fuels. The use as innocent support and promoter of the kinetics of a variety of other nanomaterials is also described, completing the scenario.

Part III is entitled *Active Materials*. Chapter 7 describes the main approaches to metal nanoparticle synthesis and the main commercial electrocatalysts. A variety of nanostructured metals with shape and structure control (Chap. 8) are considered. A special emphasis is laid on control of the surface structure, with a discussion of the recent discovery of new synthetic routes to high index faceting for activity enhancement. Chapter 9 reports classes of nanoparticles engineered for the reduction of noble metal loading. The focus is on “hollow” and “core” shell nanoparticles. Chapter 10 reports a “molecular” approach to electrocatalysis. The use of macrocycles and heat treated macrocycles in electrocatalysis is extensively reviewed with a special emphasis on the most recent findings. The description of the breakthrough discovery of organometallic complexes employed in electrocatalysis is also given. The objective is to provide examples of single site processes leading to a completely new approach which could be considered to go “beyond nanotechnology.” A short conclusion summarizing the main aspects of each single material category is then reported in Chap. 11.
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Lavacchi, A.; Miller, H.; Vizza, F.
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