Edited by Ali Eftekhari

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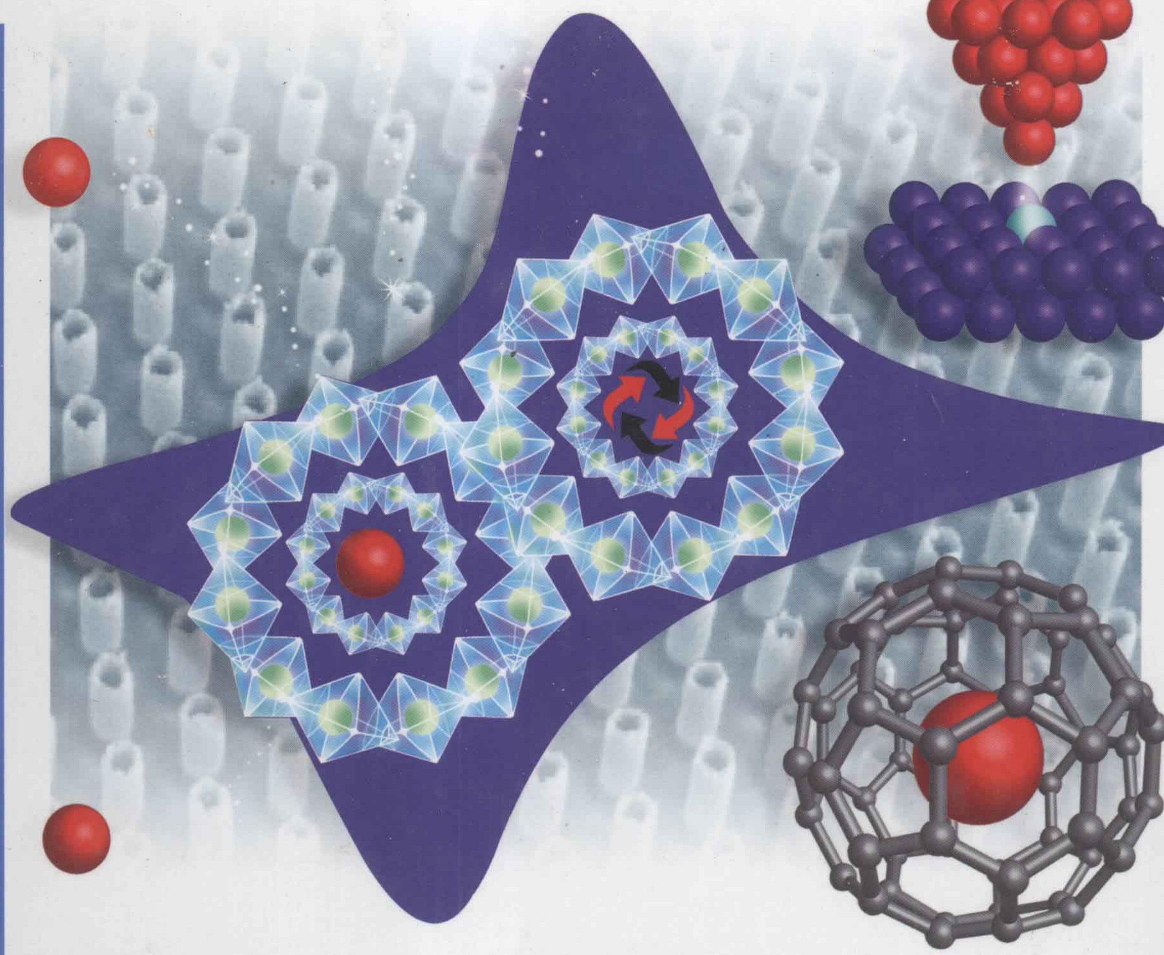
Nanostructured Materials in Electrochemistry



Nanostructured Materials in Electrochemistry

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The Editor

Dr. Ali Eftekhari
Avicenna Institute of Technology
Cleveland, Ohio
USA

Cover Description
Center: In solid-state electrochemistry, the shape of a cyclic voltammogram depends on numerous complicated processes occurring simultaneously, and the cyclovoltammogram is its statistical representative. Bottom right: Fullerenes have also garnered interest for electrochemical nanotechnology as cages in which ions can be trapped. Top right: The classic scheme of the tunneling effect as the basis of scanning tunneling microscopy (STM) is shown, which is capable of visualizing the occurrence of various electrochemical processes at the electrode surface and has also inspired scanning electrochemical microscopy (SECM).
Original artwork by Ali Eftekhari, adapted by Bernd Adam.

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Further Reading

Zehetbauer, M. J., Zhu, Y. T. (Eds.)

Bulk Nanostructured Materials

2008

ISBN: 978-3-527-31524-6

Bard, A. J., Stratmann, M. (Eds.)

Encyclopedia of Electrochemistry

11 Volume Set

2007

ISBN: 978-3-527-30250-5

Hamann, C. H., Hamnett, A., Vielstich, W.

Electrochemistry

2007

ISBN: 978-3-527-31069-2

Wang, J.

Analytical Electrochemistry

2006

ISBN: 978-0-471-67879-3

Samori, P. (Ed.)

Scanning Probe Microscopies Beyond Imaging

Manipulation of Molecules and Nanostructures

2006

ISBN: 978-3-527-31269-6

Vollath, D.

Nanomaterials

An Introduction to Synthesis, Charaterization and Processing

2008

ISBN: 978-3-527-31531-4

Rao, C. N. R., Müller, A., Cheetham, A. K. (Eds.)

Nanomaterials Chemistry

Recent Developments and New Directions

2007

ISBN: 978-3-527-31664-9

Foreword by R. Alkire

Electrochemical phenomena control the existence and movement of charged species in the bulk phases as well as across interfaces between ionic, electronic, semiconductor, photonic, and dielectric materials. During the past several decades, the study of electrochemical phenomena has advanced rapidly owing, in large part, to the invention of a suite of new scientific tools. Electrochemical processes have thus provided the ability to create precisely characterized systems for fundamental study. Usage includes the monitoring of behavior at unprecedented levels of sensitivity, atomic resolution, and chemical specificity and the prediction of behavior using new theories and improved computational abilities. These capabilities have revolutionized fundamental understanding, as well as contributed to the rapid pace of discovery of novel material structures, devices, and systems.

This volume, "*Nanostructured Materials in Electrochemistry,*" focuses on the importance of electrochemistry in the fabrication as well as the functional capabilities of a great many nanostructured materials, processes and devices. It provides an authoritative overview of a dozen key topics contributed by leading experts from academic, industrial, federal and private research institutions located around the world. The viewpoints of the authors arise from a variety of disciplines that span science, mathematics, and engineering. Of particular note are the references to the recent literature, more than 2100, which has grown exponentially since the mid-1990's.

Interwoven throughout the chapters of this work are several overarching themes that, taken together, provide a strategic framework for closing the gap between nanoscience and nanotechnology. These include:

Open-ended Discovery and Targeted Design

Open-ended curiosity-driven research and discovery at the nanoscale has established a spectacular record of success, based in large part to the availability of a multiplicity of experimental methods and data assimilation/visualization tools that provide broad access and the development of informed intuition. Targeted design builds on the foundation of curiosity-driven discoveries, but involves working backward from the desired function or product to perfect the underlying material and the process conditions by which it can be fabricated. This volume expands the common ground between these approaches, both of which are essential. A particularly valuable contribution of this volume is the identification of numerous "model" systems which

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have been found to provide consistent results suitable for developing refined scientific experiments, as well as for establishing robust well-engineered systems that work.

The Flow of Information between Individuals both Within and Amongst Disciplines

The ease with which new results and insights are used by specialists working on other aspects of a related problem is extremely important for the integration of shared purposes across disciplines. Clearly evident in this volume are many examples of how critical knowledge is shared amongst specialists working together to transfer innovative ideas and insights into new products and processes. These examples serve to emphasize the importance of reporting results in ways that others can not only use them, but can also modify them for other purposes.

Multi-scale Phenomena

New applications of novel materials and devices are being discovered where the critical functional events depend upon the control of structure at the nanoscale, while the product fabrication is controlled by macroscopic variables. The examples in this volume can serve to inspire the creation of new process engineering methods to ensure product quality in complex, multi-scale, multi-phenomena systems.

Collaborative Environment

The scientific discoveries described in this volume are leading inexorably to new technological advances, the manufacturability of which requires precise quantitative understanding at a magnitude, sophistication, and completeness that is extraordinarily difficult to assemble today. Methods for collaborative discovery and problem-solving across disciplines today are in their infancy. The pioneering efforts reported in this volume provide the breeding ground for the particular applications at hand.

The editor has assembled a group of chapters that provide excellent coverage of the literature and tutorial background in addition to details direct from the authors' own experience. The chapters include numerous examples of methods and merits of various electrochemical and other procedures for the formation of nanostructured materials which have a wide range of forms and combinations of properties; the effect of electrochemical processing conditions on morphology, structure, reactivity and properties with numerous discussions of mechanistic aspects and the novel devices which result. These include devices based on ultra-small electrodes and sensors; nanocomposites and alloys for energy storage; photoelectrochemically active nanoparticles for batteries and solar cells; nanostructured interfaces for biosensors; and noble metal nanoparticles for electroanalytical applications.

The volume represents a benchmark for the current state-of-the-art, and provides numerous paths by which nanoscale science and technology is moving from an art form into the science and technology of well-engineered devices and products. The contents describe generic approaches that have the potential to contribute well beyond the specific systems used here.

December 2007

Richard Alkire
Charles and Dorothy Prizer Professor
Department of Chemical and Biomolecular Engineering
University of Illinois, Urbana, USA

Foreword by Y. Gogotsi and P. Simon

Nanostructured materials or nanomaterials – which are materials with structural units on a nanometer scale in at least one direction – have received much attention worldwide over the past decade. Indeed, for just one single class of nanostructured materials – the carbon nanotubes – the number of published reports has increased from less than 500 per year in 2000 to almost 3000 in 2007 (ISI Web of Science). Since material properties become different on the nanoscale, much effort is currently being dedicated to the synthesis, structure control and property improvement of nanomaterials. For example, the deformation mechanisms of nanocrystalline metals are different from those of microcrystalline metals. One-dimensional nanomaterials such as nanotubes and nanowires possess many attractive properties which can be fine-tuned by controlling their diameter. Today, the industrial applications of nanomaterials continue to grow in number, with hundreds of products now available worldwide. Nanostructured materials are widely used in many applications where people do not expect to see nanotechnology. An average reader of this book will probably know that the huge storage capacity of a computer hard drive is achieved thanks to nanosized magnetic particles, and that a diamond-like carbon coatings of a few nanometers thickness protects the surface of the magnetic head which is reading the hard drive. However, few people realize that when they make an omelet on an aluminum frying pan they benefit from an anodic alumina coating of less than 100 nm thickness with well-aligned cylindrical pores of less than 20 nm diameter, whether they use a non-stick Teflon-coated frying pan or professional-grade cookware with no Teflon coating. These coatings are produced by an electrochemical process – the anodization of alumina – and are widely used to provide protection and/or give specific colors to aluminum surfaces. On the other hand, anodic alumina films (membranes) are widely used as templates for producing metal nanowires, carbon nanotubes and other elongated nanostructures. These examples demonstrate the clear synergy that exists between nanomaterials and electrochemistry.

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Nanostructured materials have also led to major advances in electrochemical energy storage areas and, more specifically, to lithium-ion batteries. The recent discovery of the universal "conversion reaction" mechanism, which involves the formation of nanosized metal particles, is an excellent example of a breakthrough that has been achieved due to nanotechnology. Moreover, today the nanosize dimension makes it possible to use materials that once were considered useless for battery applications. The best illustration of this is carbon-coated nano $LiFePO_4$, which, today, is one of the most widely studied materials for positive electrodes of lithium-ion batteries.

Nanostructured materials also promise to revolutionize the field of supercapacitors, thus opening the doors to many applications, such as Hybrid Electric Vehicles (HEV) and portable electronic devices. Unfortunately, however, the fields of materials and electrochemistry are not necessarily well connected – many materials scientists do not receive any formal training in electrochemistry during their undergraduate (and even graduate) education, while most chemists have only a limited knowledge of the structure–property relationships of materials. Therefore, a book addressing both communities – and written by research scientists with backgrounds in both chemistry and materials – should prove to be very useful for those who produce nanomaterials using electrochemistry methods, who study the electrochemical behavior of nanomaterials, or develop materials for electrochemical applications.

The chapters of this book describe the preparation of anodic alumina membranes, the preparation of nanopatterned electrodes, the use of porous alumina and polycarbonate templates for synthesis of nanowires, and the electrochemical deposition of nanostructured oxide and metal coatings with different morphologies, as well as the use of nanoparticles and nanomaterials in lithium-ion batteries, hydrogen storage, solar cells, biosensors, and electroanalysis. Whilst the area addressed by the book is very broad, it is hardly possible to cover all nanomaterials for all electrochemical applications in a single volume. Hence, metals have received more attention than carbon nanomaterials; while materials for batteries are described in two chapters materials for supercapacitors and fuel cells did not receive equal attention. However, overall, a wide range of topics has been addressed and the book content certainly corresponds to its title.

This book has been written for today's scientists, graduate students and engineering professionals in order to provide an overview of nanostructured materials and electrochemical techniques and applications. The book consists of 12 chapters written by researchers representing a wide geographic spectrum. It provides coverage of the latest developments in the United States, Western Europe, and Japan, as well as of investigations conducted in Brazil and Eastern European countries, which received less attention in previous volumes on nanomaterials, such as the *Nanomaterials Handbook*, edited by Y. Gogotsi (CRC Press, 2006). We are confident that many readers will find interesting reviews covering a broad range of subjects in this interdisciplinary volume.

November 2007

Yury Gogotsi[1)]
Professor of Materials Science and Engineering
Drexel University
and
Director, A.J. Drexel Nanotechnology Institute,
Philadelphia, PA, USA

Patrice Simon[2)]
Professor of Materials Science
Paul Sabatier University
Toulouse, France

1) Y.G. has a MS degree in metallurgy, PhD in physical chemistry and DSc in materials engineering, but considers himself a material scientist.

2) P.S. has a BS and MS in Chemistry and Physics, and a PhD in materials science, but considers himself an electrochemist.

They work together to solve problems at the interface between materials science and electrochemistry.

Preface

The interaction of electrochemistry and nanotechnology has two sides, namely the applications of nanotechnology in electrochemistry, and vice versa. Although, as inferred by the title, this book deals with the former subject, the basic concept behind it was to unite the two sides of this newly born field, which we can then refer to as Electrochemical Nanotechnology. Due to vast range of topics in this field, there was a clear obligation to focus on only a part of the field, and hence this book is not considered to be an exhaustive resource on the subject, but rather to provide some important information on a variety of topics that will attract the attention of readers to current issues in the subject. In my opinion, such a united volume is indeed capable of providing a comprehensive perspective of the whole field. After undergoing rapid and growing specialization during the past few decades, now is the time for interdisciplinary studies and collaboration between the various fields. Today, the successful research groups are those which conduct studies that are significant and important not only for the people working within the field, but also for those working in other areas. Here, nanotechnology represents a vivid example, as the extreme success of this newborn field is due as much to the generality of its findings as to the interest of the research teams working in its various areas.

The reason why such emphasis is placed on Electrochemical Nanotechnology is due not only to the existence of so many interesting topics within the category, but also to its important concepts. Today, many research groups working in nanotechnology also have wider interests in electrochemistry, as electrochemical methods are typically low-cost and also highly effective for the preparation of nanostructures. This newfound attention is due largely to the methodology employed, which may also be used for fundamental studies. In fact, rather than electrochemistry being considered as a branch of chemistry, its footprints can be seen in a variety of fields for both methodological applications and fundamental studies. For example, when studying chaotic dynamics in chemical systems, electrochemical oscillators provide the best means of proposing general models, as both controllable parameters and system response form part of the electrochemical set-up. Indeed, this is also the case for nanotechnology.

The reason why I first came to the field of nanotechnology stemmed in fact from my studies in electrochemistry – it was not the "fame" of nanotechnology, because in

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those days the subject was not famous! My first encounter with the subject occurred while studying electrochemical oscillations, when I noticed a classic theory that the distribution of potential is inhomogeneous across the electrode surface. So, I thought that it might be very interesting to identify a way in which the local currents on an electrode surface could be inspected. Subsequently, the invention of the scanning electrochemical microscope (SECM) paved the path to this goal. My second encounter occurred when I tried to use carbon nanotubes as the anode material of a lithium battery, and I had considered preparing separate sheets of graphene (not rolled as nanotubes), as solid-state diffusion within graphite interlayers occurred so slowly. Although neither of these topics has yet been fully addressed, these early calls for nanotechnology within the realms of electrochemistry were due to the essential role of nanoscale in electrochemical systems.

The SECM is commonly considered as a form of scanning probe microscopy (SPM), and is of major interest to electrochemists. In fact, opinion suggests SECM is an advanced form of SPM, as it provides the great opportunity to control not only (electro)chemical processes but also the common applications of SPM (here, I am not talking about the features of currently available commercial microscopes, but rather the concepts involved). Unfortunately, non-electrochemists are often afraid to use the SECM due to the existence of strange electrochemical processes that may affect their results. There is, therefore, a clear need for scientific collaboration, rather than simply ignoring these great opportunities. In the second case, as well as using electrolysis to prepare graphene sheets by simply cutting a graphite electrode layer-by-layer, the opportunity exists to examine these nanomaterials by using electrochemical methods, rather than by their applications. In this respect, recent advances in methods such as fast voltammetry have provided new opportunities in surface electrochemistry, mainly in the identification of nanostructures.

Richard Alkire has well described the journey of electrochemistry towards nanotechnology and summarized the contents of this book upon this connection. The present book deals with the area of Electrochemical Nanotechnology where nanomaterials are applied in electrochemical systems. Yury Gogotsi and Patrice Simon expressed the rapidly growing applications of nanotechnology in our everyday life as electrochemistry is an important part of such industries, and also the server need of nanotechnology in modern electrochemistry (e.g., electrochemical power sources). However, such mutual involvements are not vivid to both parties. In fact, the book's contents describe the importance of nanostructured materials in electrochemical systems, and the value of electrochemical methods in the preparation of nanostructures.

At this point the reader may wonder why I so frequently place emphasis on Electrochemical Nanotechnology, when in fact the book does not comprehensively cover all aspects of the subject. The main mission of books such as this is to review certain "hot" topics within specified areas of research – something that review articles in scholarly journals often cannot do because they are published in a too-general or too-specialized medium. In this regard, electrochemical materials science is of particular interest due to a very broad readership since, within the electrochemical literature, most studies are associated with materials science, and numerous electrochemical studies are also reported in the materials science literature. Yet, according to the similarities of the electrochemical processes (both in applications and synthesis), it is very useful for the different research groups to know similar systems. Consequently, in order to address so many different aspects of the subject under consideration, a variety of current topics that should be of interest to all readers are discussed.

Today, perhaps the main emphasis in the rapidly growing field of Electrochemical Nanotechnology is to identify a new way of thinking. However, whilst all fields of science have their own "jargon", it is clearly more important to devise a consistent method of thinking rather than a unique terminology. Moreover, such concerted effort should lead to a united scientific community, which is essential for the advancement of any field of investigation. Within the realms of Electrochemical Nanotechnology, researchers of different training and thought methods are becoming increasingly involved, and this can surely only prove to be advantageous for the subject in the long term.

It is hoped that, although similar volumes have been produced in the past, this book will attract the attention of many research groups, who hopefully will unite in their studies of the general features of this new area. Undoubtedly, such a situation will not only result in a more comprehensive realization of the subject, but also lead to improved problem-solving capabilities in the field of Electrochemical Nanotechnology.

The realm of Electrochemical Nanotechnology in fact consists of a broad range of topics, hence leading researchers from various areas of study were involved in this book project. They address the most fascinating current issues and challenges that have presented themselves at the interface of electrochemistry and nanotechnology. Though coming from various different backgrounds in electrochemistry or materials science, the authors share a joint belief that the essential link between electrochemistry and nanotechnology has previously been missing, and must now be tackled.

It is my great pleasure and good fortune to have two invaluable forewords by three highly esteemed scientists. As a leading electrochemist, the fame of Richard Alkire is due to his considerable contributions to the fundamentals of electrochemistry, and in this capacity he has also contributed brilliantly to the fundamental aspects of Electrochemical Nanotechnology, in particular electrodeposition.

Yury Gogotsi is one of the leading scientists in nanomaterials, and has carried out groundbreaking work on numerous types of nanomaterials, especially carboneous ones. His collaboration with Patrice Simon is an example of the need for the combination of electrochemistry with nanotechnology, which cannot be emphasized often enough.

Last but not least, I would like to note my appreciation of the Wiley-VCH editors' foresight in picking out this particular topic and their kind efforts which made the publication of this book possible. I wish to thank them for their essential roles.

I sincerely hope that the readers find the contents of this work useful for their scientific research.

January 2008 *Ali Eftekhari*

List of Contributors

Katerina E. Aifantis
Aristotle University of Thessaloniki
Lab of Mechanics and Materials
Box 468
54124 Thessaloniki
Greece

Damien W. M. Arrigan
University College
Tyndall National Institute
Lee Maltings
Cork
Ireland

Aurelien Du Pasquier
Rutgers, The State University of New Jersey
Department of Materials Science and Engineering
Energy Storage Research Group
671, Highway 1
North Brunswick NJ 08902
USA

Nelson Durán
Universidade Estadual de Campinas
Instituto de Química
P.O. Box 6154
13083-970, Campinas, SP
Brazil

Omar Elkedim
Université de Technologie de Belfort-Montbéliard
Génie Mécanique et Conception
Rue du Château
90010 Belfort cedex
France

Adriana Ferancová
Slovak University of Technology
Faculty of Chemical and Food Technology
Institute of Analytical Chemistry
Radlinského 9
81237 Bratislava
Slovakia

Renato G. Freitas
Universidade Federal de São Carlos
Departamento de Química
CX.P.: 676
13560-970. São Carlos, SP
Brazil

Stephen A. Hackney
Michigan Technological University
Department of Materials Science and Engineering
1400 Townsend Drive
Houghton, MI 49931
USA

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Mieczyslaw Jurczyk
Poznan University of Technology
Institute of Materials Science and Engineering
Sklodowska-Curie 5 Sq.
60-965 Poznan
Poland

Ján Labuda
Slovak University of Technology
Faculty of Chemical and Food Technology
Institute of Analytical Chemistry
Radlinského 9
81237 Bratislava
Slovakia

Yvonne H. Lanyon
University College
Tyndall National Institute
Lee Maltings
Cork
Ireland

Current Address

Stirling Medical Innovations Ltd.
FK9 4NF
United Kingdom

Nathan S. Lawrence
Schlumberger Cambridge Research
High Cross
Madingley Road
Cambridge CB3 0EL
United Kingdom

Han-Pu Liang
Schlumberger Cambridge Research
High Cross
Madingley Road
Cambridge CB3 0EL
United Kingdom

Luiz H.C. Mattoso
EMBRAPA-CNPDIA
Rua XV de Novembro, 1452
São Carlos
13560-970 São Carlos, SP
Brazil

Shuji Nakanishi
Osaka University
Graduate School of Engineering Science
Division of Chemistry
1-3 Machikaneyama, Toyonaka
Osaka 560-8631
Japan

Marek Nowak
Poznan University of Technology
Institute of Materials Science and Engineering
Sklodowska-Curie 5 Sq.
60-965 Poznan
Poland

Cristiane P. Oliveira
Universidade Federal de São Carlos
Departamento de Química
CX.P.: 676
13560-970 São Carlos, SP
Brazil

Arnaldo C. Pereira
Universidade Estadual de Campinas
Instituto de Química
P.O. Box 6154
13083-970, Campinas, SP
Brazil

Ernesto C. Pereira
Universidade Federal de São Carlos
Departamento de Química
CX.P.: 676
13560-970 São Carlos, SP
Brazil

Mattias Strömberg
Uppsala University
Department of Engineering Sciences
Division of Solid State Physics
The Ångström Laboratory
Box 534
Lägerhyddsvägen 1
751 21 Uppsala
Sweden

Maria Strømme
Uppsala University
Department of Engineering Sciences
Division of Solid State Physics
The Ångström Laboratory
Box 534
Lägerhyddsvägen 1
751 21 Uppsala
Sweden

Grzegorz D. Sulka
Jagiellonian University
Department of Physical Chemistry and
Electrochemistry
Ingardena 3
30060 Krakow
Poland

Sima Valizadeh
Uppsala University
Department of Engineering Sciences
Division of Solid State Physics
The Ångström Laboratory
Box 534
Lägerhyddsvägen 1
751 21 Uppsala
Sweden

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