Electrochemical Methods for the Synthesis and Analysis of Advanced Functional Layers and Coatings

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Edited by

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SAMANTHA L. FLORES-LÓPEZ, LUCÍA DOS SANTOS-GÓMEZ,
ANA ARENILLAS, NATALIA REY-RAAP

CURRICULUM VITAE

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He acquired his Ph.D. degree in 2010, with a specialty in the field of: *technology of silicates, binding materials and high temperature-fusible non-metallic materials*, at the University of Chemical Technology and Metallurgy (UCTM)–Sofia, (Bulgaria). His doctoral thesis was entitled: "*Investigation and evaluation of nano-composite hybrid coatings for corrosion protection*". He acquired his M.S. degree in Chemical Engineering in 2004 from the Faculty of Metallurgy and Material Sciences at UCTM–Sofia, with a specialty in Silicate materials, and the title of his thesis was: *Elaboration and characterization of red ceramic pigments with perovskite structure*, presented also in UJI – Castellon (Spain). His B.Sc. thesis was presented in 2002 in the same University, and it was devoted to: "*Sterilization of drink water by immobilized photosensitizers*". Nowadays, he is an author of 8 book chapters and more than 70 publications (h-index 13 and 660 citations), related to advanced corrosion protection systems, ceramic materials recycling, spray pyrolysis synthesis and ceramic sensor elements elaboration.

Until now, he has been an active participant in 4 international research projects and 10 research projects, with financial support from the National Scientific Research Fund of Bulgaria.

PREFACE

Electrochemistry is a continuously extending field, including recently organic and hybrid compounds, as well as high voltage and/or precisely modulated signals. That is the reason for the intensive world-wide research work, devoted to the elaboration of nanostructured functional films and multilayer systems. During the last century, the main objective of the electrochemical film deposition technologies was the development of the classical direct current favored galvanic deposition methods. Nowadays, these methods are objects of further improvement, by addition of detergents and other additives, the use of precisely modulated impulse series and high frequency AC-signals, etc. Besides, the recent environmental restrictions have imposed the substitution of highly toxic electrolytes, like the cyanide and chromate-based ones with more suitable electrolyte compositions. This trend extends to the avoidance of concentrated volatile acid solutions, like H_2SO_4 which evolves SO_3 during the film deposition. An excellent example in this sense is the increasing number of publications, dedicated to the anodization and *plasma electrolytic oxidation* (PEO) of metals, like aluminum, titanium, copper, etc., in environmentally friendly electrolytes. The great interest for modification of these classical methods is the multiple evinced ease control of the resulting porosity. This fact enables the elaboration of non-defective, high textured layers for various high-tech applications. The recent main trend of the electrochemical film deposition methods is related to the use of completely new classes of compounds, such as metal alkoxides, or biocompatible amino acids, etc.

All the tendencies mentioned above predetermine entire fields of the application of the resulting electrochemically synthesized films and multilayered systems predetermine their potential applications in key-branches of the modern hi-tech industry, such as:

(i)- Advanced corrosion protective layers;

(ii)- Electrodes and solid-state electrolytes for fuel cells

(iii)- Layered photovoltaic components and full assemblies

(iv)- Layered *Metal-Oxide-Semiconductor* (MOS) systems for the need of microelectronics and communications;

(v)- Advanced catalysts and photocatalysts for chemical synthesis and contaminant decomposition;

(vi)- Thin layer electrochemical sensors and detectors for modern industrial automation and environment monitoring;

(vii)- Membrane technologies for medical and environmental purposes, etc.

The industrial production of any product can be considered as a complete conversion of raw and/or recycled materials into a product with a desirable composition, structure, and properties. It consists of consecutive execution of technological operations, by various methods, performed under appropriate conditions with suitable equipment, material and energy sources.

All the electrochemical methods are based on electrochemical synthesis reactions. These reactions can be considered as specific oxidation/reduction ones, which always proceed by an electron charge transfer across an electrode/electrolyte interface. Hence, their mechanism is predetermined by their heterogeneous character, consisting of:

(i) Diffusion of electroactive species in the electrolyte bulk

(ii) Adsorption on the electrode surface

(iii) Charge transfer (namely, the electrochemical reactions)

(iv) Either product desorption (when nanopowders are produced) or product film growth (when the purpose is layers and coatings)

In this sense, electrochemistry provides a variety of possible technological processes for the formation of thin films and even multilayered systems on various electroconductive solid surfaces. All these electrochemical methods are always based on electrochemical reactions between the solid electrode and the surrounding electrolyte. The mechanisms of these reactions can be summarized as the electrochemical oxidation or reduction of the compounds near the electrode/electrolyte interface. These reactions always proceed with a charge transfer across the interface. Another distinguishable feature of the electrochemical film formation processes is that the electrochemical cells (i.e. electrode/electrolyte conjunctions) always serve as electrolytic elements.

This fact means that the electrochemical film formation reactions proceed by consumption of electrical energy. Consequently, the conductive substrates must be polarized by the input of electromotive potential from an external source of electricity. Thus, the substrates for film deposition serve as *working electrodes* (WE). The respective counter electrodes are usually composed by noble metals like Pt, in order to avoid any fluctuations of the chemical composition on their surface. In some cases, especially in the large-scale industrial sector, the counter electrodes can be made from stainless steel or graphite, due to economic considerations. Such prevention of the counter electrode surface composition results in the keeping of its surface area from any undesirable corrosion product or non-conductive layer coverage or electrode dissolution.

In such film formation electrochemical cells, the film deposition substrate serves as an electrically polarized electrode. If it is polarized negatively, then it attracts cations from electrolytes and provides electrons for their oxidation. This approach stays on the basis of practically all types of galvanic coatings. The most widely spread galvanic coatings are the zinc, nickel and chromium protective layers for the corrosion protection of iron-based materials. Although the galvanic deposition of metals on other metals is a well-known practice, it continues to be the object of optimization through the removal of toxic and environmentally unacceptable electrolyte ingredients, in addition to organic compounds, like surfactants, detergents or pH buffers and the application of modulated electric signals, which enable relaxation of the substrate and so on.

Other fields of electrochemical film formation by cathodic polarization are the formation of lanthanide and especially *cerium oxide primer layers* (CeOPL) as an ecological alternative to the already banned *chromium conversion coatings* (CCC), the electrochemical deposition of various organic and hybrid compounds, etc.

On the other hand, the electrochemical film formation (through positive polarization of the metallic substrate) provides other well-known electrochemical methods, like anodization and plasma electrolytic oxidation. In these cases, the resulting film grows in account of surface oxidation of the substrate material. The resulting oxide layers possess rather high textured surface topology, complete coverage of the immersed WE surface and inherent properties, repeatability on the entire electrode surface and reproducibility after multiple repetitions of the process on various samples.

Another advantage of these films and especially of the *anodized aluminum oxide* (AAO) layers is their aptitude to be electrochemically modified by re-anodization or by metal incorporation with various possible regimes and electrolytes. This approach renders great potential for the growth of dense protective oxide layers with enhanced chemical stability and mechanical strength, *metal oxide semiconductor* (MOS) layers formation, etc.

Recently, various authors have investigated the possibility of film formation via the application of an altering current, which enables the triggering of subsequent different processes, which influence the resulting film morphology.

Among the electrochemical film formation methods, electrophoresis enables the use of electrically charged organic moieties, like amino acids, large chain organic acids and their salts, hydroxyl and amino silanes, siloxanes, organic hydroxide and carboxide derivates, etc.

Finally, another class of electrochemical film formation methods is the spontaneous electrochemical deposition by autophoresis, etc.

Recently, the interest to these electrochemical deposition methods will undoubtedly increase, due to the recently synthesized organic conductive materials, like polyanilines, polypyrroles, porphyrins, phthalocyanines etc., which can be used as a deposition substrate or electrolyte components.

Finally, all these aspects of optimization of classical film deposition processes and the elaboration of completely new types and entire classes of thin layers and multilayered systems predetermine the great potential interest of various researchers from the entire world.

In general, the electrophoretic and autophoretic methods differ from other electrochemical film formation methods, the electrolyte is colloidal suspension and the charged particles are macromolecules or fine dispersed solid particles. This fact enables the use of a great variety of potential precursors for the deposition of relatively thicker protective films.

Following the classical concepts of electrochemistry, related to film formation on pure metallic surfaces, the film growth can be easily calculated by the Laws of *Faraday*. Thus, for metallic ions deposition, the quantity n of deposited metal (Me) from its ions (Me^{+v}), following reaction (1):

$$Me^{+v} + \nu e^{-} = Me^{0} \qquad (1)$$

Consequently, the weight $\boldsymbol{m}$ of the deposited metal, with the defined atomic weight $\boldsymbol{M}$ can be calculated by the current $\boldsymbol{i}$, applied for a given time $\boldsymbol{t}$, across a contact surface $\boldsymbol{S}$, knowing $\boldsymbol{F}$ – Faraday constant; and the number of electron exchanges during the reaction:

$$m = \frac{i.t.M}{F.S.\upsilon} \qquad (2)$$

Nevertheless, every electrochemical reaction is coincided by multiple coinciding reactions, which also consume electric current. Such coinciding reactions are water splitting, and the resulting hydrogen and oxygen evolution, electrochemical reduction or oxidation of other components of the electrolyte or the substrate alloy. Among the most typical examples of coinciding reactions is the pore formation during the anodization of aluminum. Namely, this process is a result of partial AAO layer dissolution coinciding with the layer growth. The coexistence of formation and partial dissolution results in the typical high textured AAO layer topologies.

This coexistence of a multitude of reactions is the main reason for the need for detailed investigations on film grow kinetics, since the real film growth rate is always rather lower than the theoretical one. The investigations should also include a detailed characterization of the obtained film's compositional, structural, and properties.

In this sense, the proposed book should serve as a valuable source for a description of the approaches necessary to apply for detailed film deposition mechanisms and their impact on characteristics of the obtained coatings and layers.

Indeed, the conjunction among the structure, composition, form (i.e. topology, porosity, etc.) and the resulting film properties, like density, mechanical strength, conductivity, etc., is entirely predetermined by the applied film formation method and conditions.

The majority of the scientific research works devoted to electrochemical film formation is dedicated to the description of the correlation between the applied film synthesis conditions and the resulting film properties.

In general, among the most intensively investigated fields is the corrosion protection of the electrochemically deposited coatings and layers on various metallic substrates.

The electrochemical film formation and conditions, which can be the potential object of research, impact directly on the electrode/electrolyte interface. Consequently, the research activities are devoted to the components of this interface, as follows:

(i) Basic substrate alloy composition

(ii) Topology of the metallic surface and its alteration before and after the film formation

(iii) Ionic and electron conductivity of the growing layer

(iv) Composition of the electrolyte, including the basic ingredient concentration and the addition of supplemental compounds.

(iv) Electric signal types, like potentiostatic, galvanostatic, AC or modulated impulse deposition.

(v) Values of the input electric signals which predetermine the current density across the electrode/electrolyte interface.

(vi) Process continuation, which predetermines the total electric charge passed through the electrode/electrolyte interface, until the achievement of the final thickness of the resulting film.

(vii) Other important factors such as process temperature, electrolyte pH, hydrodynamic regime, etc.

The combination of all these conditions entirely predetermines the type of the resulting coating, and must be taken into account prior to the elaboration of any electrochemical film deposition method. In this sense, the proposed book will be a valuable guide for young researchers, devoted to various fields of material science. That is the reason for the need for special Chapters, related to the elaboration of functional coatings with defined purposes:

For instance, among the main reasons for intensive research activities, related to the electrochemical deposition of corrosion protective layers is the imposed conjunction of requirements, which needs to be covered. Thus, recently, besides the need for high density, adhesion to the substrate, mechanical strength and chemical stability, the coatings need to possess capability for active corrosion protection. In this case, the deposited layer should possess self-healing abilities.

The electrochemical sciences combine the knowledge of electrochemical film deposition and the application of the already formed layers for multilayered alternative energy sources, like fuel cells and light assisted water splitters and energy carriers, such as supercapacitors, lithium ion, or Zn-air batteries.

Alternatively, the combination of Al anodization and electrochemical transition or noble metal incorporation in the pores of the resulting anodic oxide films enables the creation of a variety of efficient catalysts or electrocatalysts for chemical synthesis or environment contaminants decomposition. Besides, other metals like Zn also could be anodized.

Furthermore, the anodization followed by the separation of the obtained oxide layers from the metallic substrates enables the creation of semipermeable membranes with exactly defined porosity, and with remarkable repeatability rate, with potential medical, environmental and industrial applications.

Another important potential field of use of the electrodeposited thin layers is in the active components of sensors and detectors. Their use is continuously increasing, because of the needs for environmental monitoring in urban conditions and industrial plants. Another main field of sensor and detector use is in the medical application for quick diagnostics of various diseases.

The present book is an attempt at the versatile comprising of all theoretical and practical aspects, related to both the film deposition and analysis of the electrochemical properties of the obtained layers and coatings. Besides, as an additional expected benefit of the proposed book, it should be a valuable literature source for scientific researchers from different material science fields and from the real industrial sector. Furthermore, the proposed book should unite the distinguishable features of the scientific and educational literature, which in general, are rather different, due to their distinguishable purposes (i.e., the former aim to introduce young specialists and students to the established, well-known laws, concepts and practices of electrochemistry, whereas the latter is targeted to the experienced specialists and only to the recent ascents of research activities).

Combining both of these types of literature, the proposed book should be addressed to as large a number of potential readers as possible. Indeed, the proposed concept is addressed to completely different target groups from the scientific research media, the real (industrial) sector and the representatives of the educational sector, including even high schools.

Finally, the editor acknowledges Contract **№: BG-RRP-2.004-0002-C01**, project name: **BiOrgaMCT**, Procedure **BG-RRP-2.004** “Establishing of a network of research higher education institutions in Bulgaria” for the financial support of the initial book draft preparation. **INFRAMAT**, distributed research infrastructure of the National Roadmap for Scientific Infrastructure is acknowledged as well.

Besides, the editor likes to express his appreciation to Dr. Maria Todorova from the Department of Humanities of the University of Chemical Technology and Metallurgy – Sofia for her efforts regarding the translation of Chapters VI and IX, as well as for the grammar revision of the entire initial draft book version.

Dr. Maryia Georgieva is also acknowledged for her contribution to the quality of the present book.

INTRODUCTION

The present book, entitled: "*Electrochemical Methods for the Synthesis and Analysis of Advanced Functional Layers and Coatings*" comprises a variety of current aspects, related to the application of electrochemical methods in the realm of advanced materials synthesis and analysis. It is composed of 10 book chapters, devoted to the recent world-wide trends in material science. The content of all chapters is directed to the elaboration of advanced powder nano-materials and functional thin layers and films by application of electrochemical methods. The nano-sized powder and thin layer materials proposed by the authors possess a great potential for application in alternative energy sources, like solid oxide (SOFC) and polymer electrolyte membrane (PEMFC) fuel cells, as well as for photovoltaics (PV). Electrochemically synthesized materials with potential applications for energy storage are proposed, as well. In this sense, examples of electrochemically synthesized electrode layers for Lithium or Sodium Ion batteries Zn-Air elements and supercapacitors are provided. Besides, the attention of some authors is turned to the electrochemical synthesis of materials with potential applications in the fields of hi-tech devices and equipment, like MEMS and magnetic materials, and environmentally friendly corrosion protective coating primers and metal pretreatments, especially anodization.

Alternatively, a technology for Cu-metallization of non-conductive substrates of *acrylonitrile butadiene styrene* (ABS) and other rubbers and plastics is proposed, as well. Besides for commercial and household needs, the metallized plastics are rather interesting materials for the elaboration of alternative electrode materials, after additional copper surface treatment. Hence, in further chapters, the electrochemical coating of copper surfaces by Ni-Co, Ni-P, Co-P and Ni-Co-P alloys with rather interesting catalytic and even magnetic properties is proposed, providing some technological details of the process. The interest in Ni-P based layers is turned to the elaboration of PEMFC bipolar plate applications, after additional coating by *polytetrafluoroethylene* (PTFE). The authors represent an entire prototype sample, developed by them. The topic of the surface phosphatization is further extended by a brief study of the properties of cesium dihydrogen phosphate for the potential application for fuel cell technology. Meanwhile, anodization, as a typical representative of the electrochemical metal surface treatment approaches is proposed by two author teams. The authors turn their attention to the anodization of Zn and Al substrates. In these Chapters, the technological aspects of the process are described in detail. Particularly, the description of Al anodization process features is accomplished by the possible *anodized aluminum oxide* (AAO) sealing methods. There, the author describes various approaches for AAO sealing by conventional procedures with hot water and Cr(VI) containing solutions, compared with alternatives, such as environmentally acceptable Ce, Ni, Mo, Mn, etc., ions.

Among the electrochemical analytical methods, special attention is turned to two advanced instrumental methods: *Electrochemical Noise* (ECN) analysis, and *Electrochemical Impedance Spectroscopy* (EIS), as well as to classical potentiodynamic scanning methods (i.e. linear sweep and cyclic voltammetry). Particularly, the EIS data interpretation aspects are described in detail, turning to the attention of the basic rules of the model equivalent circuit composition. Further, it should be mentioned that all the authors' work teams have their specific contribution to the entire book content. Furthermore, all the book chapters maintain the basic concept of the book beginning from the theoretical backgrounds of the methods proposed by them and finishing with the real practical applications for the elaboration of advanced nanomaterials, and especially functional layers and coatings. Besides, the chapters composing the present book discover the continuously increasing interdisciplinarity of contemporary electrochemical science. Hence, the work teams of *Ana Arenillas* and *Elena Kalinina* discover the importance of the knowledge regarding colloidal chemistry for applied electrochemistry. Both work teams propose additional thermal treatment procedures, like microwave heating, sintering and calcination for the production of high performance nonstoichiometric ceramic nanomaterials. Moreover, their works are dedicated to the sol-gel synthesis method which has drastically enlarged the nomenclature of the newly synthesized advanced materials during the last decades. Indeed, the sol-gel synthesis method has recently enabled the development of entire new classes of materials, like *organically modified silicates* (ORMOSIL) and *organically modified ceramics* (ORMOCER). These authors turn special attention to the use of organic compounds such as electrophoretic deposition medium modifiers, such as surfactants and detergents. In such a manner, the authors represent the road for successful combination of the knowledge related to electrochemistry, organic chemistry and ceramic material sciences, discovering the interdisciplinary character of the electrophoretic deposition in the frame of nanotechnologies. The recently growing interest in the use of organic molecules for the needs of the modern electrochemistry is further extended by the research teams of *Ofeliya Kostadinova* and *Mihaela Georgieva*. The former work team discovers the rather attractive opportunity for further extension of the beneficial properties of electrode surfaces by quantum dots formation. The latter remarks on the indispensability of some organic compounds as reducing agents and layer modifiers, particularly for the metallization of plastics and rubbers. As was mentioned, the work team of *Sergio Gamboa* represents the practical results of the coating of the Ni-P treated AA6061 aluminium alloy by Teflon for the elaboration of their own advanced energy generation device. Some technological aspects of the Ni-Co alloy film formation, combined through phosphatation, are proposed by *Katya Ignatova–Atanassova*. She also remarks on the importance of some organic additives, like saccharin, urotropine and gelatin on the electrochemical Ni-Co-P films formation and the resulting layer properties and particularly, their morphology.

Other methods for Al surface treatment such as anodization and subsequent sealing, mentioned above, are proposed and described in detail by *Leandro González Rovira*. He pays special attention to the use of the EIS method and the related correct data interpretation rules. The topic of Zn anodization is developed by the work team of *Emil Lilov*. These authors describe the impact of various electrolyte compositions and electric regimes on the morphology and properties of the obtained ZnO films and nanoparticles.

The book finishes with a brief study performed by the work team of *Bruno Miguel Gonçalves Melo* on the protonic conductivity of cesium dihydrogen phosphate and the impact of dehydration on this property. The authors pay special attention to the EIS data obtained after extended periods of exposure of this compound to 210 °C. All the names mentioned here belong to the corresponding authors, who have responded and undertaken the care for the contribution to the content of the present book, and are deserving of great appreciation for their efforts and patience. Its content is of potential interest for all researchers dedicated to the electrochemical deposition of functional layers and coatings, as well as the specialists devoted to the application of electrochemical analytical methods for layer characterization. Of course, the content of this book should serve as a basis for the elaboration of advanced lecture and specialization courses in various academic institutions around the world.

This book will undoubtedly be an object of special interest for: **(i)** young researchers, including Ph.D. and post-doc students; **(ii)** University professors, interested in actualizing their lecture courses; **(iii)** R & D centers of hi-tech companies, interested in developing thin layer systems for communication, automation and energy generation systems, like microprocessors, sensors lithium-ion batteries, supercapacitors and solar or fuel cells.

LIST OF ABBREVIATIONS

A
AA - ascorbic acid
AAO - anodized aluminum oxide
ABS - acrylonitrile butadiene styrene
AC - alternating-current electric fields
AESEC - atomic emission spectroelectrochemistry
AET - 2-aminoethanethiol
AFM - atomic force microscopy
AH - 6-amino-1-hexanol
APhS - p-aminophenyl trimethoxysilane
APST - aminopropylsilanetriol
APTES - (3-Aminopropyl)triethoxysilane
ATP - 4-aminothiophenol
APTMS - 3-acryloxypropyl trimethoxisilane

B
BAAO - barrier-type anodic aluminum oxide
BCSCuO - $BaCe_{0.8}Sm_{0.19}Cu_{0.01}O_{3-\delta}$
BCZYYbO - $BaCe_{0.5}Zr_{0.3}Y_{0.1}Yb_{0.1}O_{3-\delta}$
BCGCuO - $BaCe_{0.89}Gd_{0.1}Cu_{0.01}O_{3-\delta}$
BDT - benzenedithiol
BMMA-5 - butyl methacrylate copolymer with 5 mol.% methacrylic acid
BTA - Benzotriazole

C
CA - capping agents
CAc - chromic acid
CBC - covalent bond classification
CCE - Cathodic current efficiency
CCM - constant current mode
CDP – Cesium dihydrogen phosphate (CsH_2PO_4)
CPE – Constant Phase Element
CPM - constant potential mode
CSO - Cerium Samarium oxide $Ce_{0.8}Sm_{0.2}O_{1.9}$
CGO - Cerium Gadolinium oxide $Ce_{0.8}Gd_{0.2}O_{1.9}$

CNC - computer numerical control
CNT – carbon nanotubes
CSSBO - $Ce_{0.8}(Sm_{0.75}Sr_{0.2}Ba_{0.05})_{0.2}O_{2-\delta}$
CTAB - cetyltrimethylammonium bromide
CTAC - cetyltrimethylammonium chloride
CQD **-** colloidal quantum dots
CV - Cyclic voltammetry

D

DC - direct-current electric field
DCC - N,N′-dicyclohexylcarbodiimide
DDOA - 2,3-didecyloxyanthracene
DLVO - Derjaguin-Landau-Vervey-Overbeek theory
DMF - dimethylformamide
DMDES – dimethyldiethoxysilane
DMSO - dimethylsulfoxide
DTMS – dodecyltrimethoxysilane
DLVO **-** Derjaguin-Landau-Vervey-Overbeek theory
DSSC **-** dot sensitized solar cells
DWCNT - double-walled carbon nanotubes

E

ECM - equivalent circuit modeling
EDL - electric double layer
EDT - 1,2-ethanedithiol
EDTA - ethylenediaminetetraacetic acid
EDX or **EDS** - energy-dispersive X-ray spectroscopy
EEC - equivalent electrical circuits
EHF **-** electrohydrodynamic flow
EG - ethylene glycol
EL - electrolyser
EIS – Electrochemical Impedance Spectroscopy
EPD - electrophoretic deposition
EtOH – ethanol
ETPTCDI - Ethanethiol-perylene tetracarboxylic diimide

F

FA - formic acid
FAS **–** fluoroakylsilane
FADH$_2$ - flavin adenine dinucleotide
FESEM – field emission scanning electron microscopy

FOTS – fluorooctyltriethoxysilane
FTIR – Fourier transform infrared spectroscopy

G

GDC - gadolinium-doped ceria
GDE – gas-diffusion electrode
GLT - gelatin
GMR - giant-magneto-resistance
GO - graphene oxide
GPTMS - 3-glycidoxypropyltrimethoxysilane

H

HDA - hexadecylamine
HDN - hydrodenitrogenation
HDS - hydrodesulfurization
HER – hydrogen evolution reaction
HEMA – Hydroxyethylmethacrylate
HF - high frequencies (range)
HMDS - hexamethyldisilathiane
HMDZ - hexamethyldisilazane
HOMO - the Highest occupied molecular orbital
HOR – hydrogen oxidation reaction
HPLC - High-performance liquid chromatography
HTAC - hexadecyltrimethylammonium chloride

I

IEP - isoelectric point
IF - intermediate frequencies
IPCCGE - incident photon to charge carrier generation efficiency
ITO - indium tin oxide
IUPAC - *International Union of Pure and Applied Chemistry*
ITFC - intermediate temperature fuel cells

L

LBNO – Ba doped $La_2NiO_{4+\delta}$
LDH - Layered Double Hydroxide
LEC - laser evaporation-condensation
LIBs - lithium-ion batteries
LF - low frequencies (range)
LPR - linear polarization resistance
LSGM - $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$

LSM - Lanthanum-Strontium Manganite
LSV - linear sweep voltammetry
LNFO - $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$
LNO - $La_2NiO_{4+\delta}$
LUMO **-** the Lowest unoccupied molecular orbital

M

MCCs - metal chalcogenide complexes
MEA - monoethanolamine
MEMS - microelectromechanical systems
MF - melamine/formaldehyde aqueous solutions
MFC - microfluidic fuel cells
MIEC - mixed ionic-electronic conductivity
MOF - metal-organic frameworks
MPA - 3-mercaptoproponoic acid
MPD - (measure) maximum power density
MPD - (compound) 2-methyl-1,3-propanediol
MTMS - methyltrimethoxysilane
MW - microwaves (including radiation field radiation, etc.).
MWCNT - multiwalled carbon nanotubes
MWH - microwave heating

N

NADH - Nicotinamide adenine dinucleotide
NIBs - Na-Ion batteries
NM - Noble metals
NMN - noble metal nanomaterial
NMA - noble metal aerogel

O

OA - oleic acid
OCP - open circuit potential
OCV - open circuit voltage
ODE - 1-octadecence
OER - oxygen evolution reaction
OLA - oleylamine
ORR - oxygen reduction reaction

P

PAA **-** polyacrylic acid
PAAO - porous anodic aluminium oxide

PAHs	-	polycyclic aromatic hydrocarbons
PAN	-	polyacrylonitrile
PB	-	polybutadiene
PCB	-	printed circuit boards
PCM	-	pulsed current mode
PDMS	-	polydimethylsiloxane
PEG	-	polyethylene glycol
PEI	-	polyethyleneimine
PEMFC	-	polymer electrolyte membrane fuel cell
PET	-	polyethylene terephthalate
PETG	-	polyethylene terephthalate glycol
PLA	-	Polylactic acid
PPD	-	P-phenylenediamine
PPM	-	pulsed potentiostatic mode
PPy	-	polypyrrole polymer
PTES	-	phenyltriethoxysilane
PTFE	-	Polytetrafluoroethylene
PTP	-	peak-to-peak (roughness measure)
PV	-	photovoltaics
PVA	-	polyvinyl alcohol
PVAc	-	polyvinyl acetate
PVB	-	polyvinyl butyral
P3HT	-	(Poly(3-hexylthiophene-2,5-diyl)) polymer

Q

QDs	-	quantum dots

R

RF	-	resorcinol/formaldehyde mixtures or gels
rGO	-	reduced graphene oxide
RMS	-	root mean square (roughness measure)

S

SA	-	sulfuric acid
SAC	-	single-atom catalysts
SAN	-	styrene acrylonitrile
SCD	-	supercritical drying
SCE	-	saturated calomel electrode
SCS	-	solution combustion synthesis
SDC	-	samarium doped ceria
SDS	-	sodium dodecyl sulphate

SEICA	**-**	solvent evaporation-induced co-assembly
SEM	-	Scanning Electron Microscopy
SHE	-	Standard hydrogen electrode
SHR	-	saccharin
SLS	**-**	sodium lauryl sulfonate
SOFC	-	solid oxide fuel cells
STM	-	scanning tunnelling microscopy
SWCNT	-	single walled carbon nanotubes

T

TAB	-	tetramethylammonium bromide
TBAI	-	tetrabutylammonium iodide
TCP	**-**	Trivalent Chromium Process
TDPA	-	tetradecylphosphonic acid
TEA	-	triethanolamine
TEOS	-	Tetraethyl orthosilicate
TEC	-	thermal expansion coefficient
TEM	-	Transmission Electron Microscopy
TFT	-	thin-film-transistor
TGA	-	(method) Thermal Gravimetric analysis
TGA	-	(compound) Thioglycolic acid
TM	-	Transition metals
TMC	**-**	transition metal carbides
TMCS	**-**	trimethylchlorosilane
TMFs	**-**	transition metal phosphides
TM-SAC	-	transition metal-based single-atom catalysts
TMN	**-**	transition metal nitrides
TMOS	-	Tetramethylorthosilicate
TOP	-	trioctylphosphine
TOPO	-	trioctylphosphine oxide
TSA	-	tartaric-sulphuric acids solution

U

URT	-	urotropine
UST	-	Ultrasound treatment
URFC	-	Unitized Regenerative Fuel Cell

X

XRF	-	X-ray fluorescence analysis
XRD	-	X-ray Diffractiometry
XPS	-	X-ray photoelectron spectroscopy

Y

YSZ	-	yttrium-stabilized zirconia

CHAPTER I

METALLIC AEROGELS FOR THEIR USE IN SUSTAINABLE ENERGY GENERATION

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I.1. Chapter preface

The current need for safe, sustainable, easily available and clean energy is one of the most pressing for our current society. The development of electrochemical devices such as fuel cells arises as the most feasible technological solution for a safe and efficient supply of energy in multiple applications. However, their widespread use still has a major impediment, which is the need for efficient catalysts that favour the reactions that take place in the fuel cell to generate energy, and that today are based on noble metals. Therefore, it is necessary to find efficient substitutes with high availability. Transition metals appear as a feasible alternative. To optimize the performance of these catalysts, it would be necessary not only to control the chemical composition but also the morphology and even to avoid, as far as possible, the use of other components as the catalyst supports. In this sense, sol-gel technology is presented as a methodology capable to produce metallic aerogels with controlled properties and with high porosity that leads to a high active surface area and therefore high catalytic activity. In this chapter, some of these metallic aerogel catalysts for electrochemical applications are presented, with special mention to innovative technological alternatives for both the synthesis of these aerogels by the sol-gel process assisted by microwave heating and the use of these aerogels in microfluidic and fuel cells devices.

I.2. Introduction

The energy demand has grown dramatically in recent decades. This is due to the constant growth of the population and our increasing dependence on electrical devices in our daily lives, a consequence of the unceasing technological development. At the same time, the importance of generating energy in a sustainable way based on renewable energy resources is already widely accepted. In this way, the energy resources would be not exhausted, and dependence on their supply would be avoided, while at the same time, it would not contribute to increasing the carbon footprint. In this context, alternative clean energy fuels have gained importance to overcome the shortage of conventional energy sources without contributing to global warming. Electrochemical devices to generate clean and sustainable energy, such as *fuel cells* (FC), have become very attractive. The currently installed FC manufacturing capacity is 11 GW, with a target of a 13 GW total installed capacity in 2023 (Hydrogen Council and McKinsey & Company 2022). There are different types of FC under constant development for performance optimization, and the classification is based mainly on the electrolyte employed and the temperature range in which the cell operates (**Table I.1**) (Mekhilef, Saidur and Safari, 2012; Tomar and Mittal, 2021).

Some examples of FC currently under development include alkaline FC (AFC) (Gülzow and Schulze, 2008; Mekhilef, Saidur and Safari, 2012), *phosphoric acid FC* (PAFC) (Acar, Beskese and Temur, 2022; Nauman Javed *et al.* 2022), *molten carbonate FC* (MCFC) (Divan, Zahedi, and Mousavi, 2022; Mehr *et al.* 2021), *direct methanol FC* (DMFC) (Alias *et al.* 2020; Ramli, Shaari and Saharuddin, 2022), *solid oxide FC* (SOFC) (Ahmad *et al.* 2022; Singh, Zappa and Comini, 2021) or proton exchange membrane FC, also known as *polymer electrolyte membrane FC* (PEMFC) (Abdelkareem *et al.* 2021; Yun Wang *et al.* 2020). In a typical fuel cell, a fuel (usually hydrogen or hydrogen precursors) is used to generate electricity through two different reduction-oxidation reactions that take place at their electrodes. These electrochemical reactions are the reduction of oxygen and the oxidation of hydrogen (ORR and HOR, respectively). Electrocatalysts must be used in order to have an efficient performance in these devices. The most common electrocatalysts are based on supported metals. Classification of the basic FC types are is shown in **Table I.1**.