MODERN ASPECTS OF ELECTROCHEMISTRY

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Applications of Electrochemistry and Nanotechnology in Biology and Medicine I



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Preface

The emergence of nanoscience and nanotechnology has led to new developments in and applications of electrochemistry. These two volumes of Modern Aspects of Electrochemistry, entitled: "Applications of Electrochemistry and Nanotechnology in Biology and Medicine, I and II" address both fundamental and practical aspects of several emerging key technologies. All Chapters were written by internationally renowned experts who are leaders in their area.

The chapter by A. Heiskanen and J. Emnéus provides a lucid and authoritative overview of electrochemical detection techniques for real-time monitoring of the dynamics of different cellular processes. First, biological phenomena such as the cellular redox environment, release of neurotransmitters and other signaling substances based on exocytosis, and cellular adhesion, are discussed thoroughly. Next, the capabilities of electrochemical amperometric and impedance spectroscopic techniques in monitoring cellular dynamics are highlighted, in comparison to optical and other techniques. The applications of such techniques already include biosensors and microchip-based biological systems for cell biological research, medical research and drug development. Finally, the state-of-the-art and future developments, e.g. miniaturization of planar interdigitated electrodes in order to achieve a gap/width size regime on the nanometer scale and thus considerable signal amplification, are summarized.

Electron transfer by thermally activated hopping through localized centers is an essential element for a broad variety of vital biological and technological processes. The use of electrode/self-assembled monolayer (SAM) assemblies to explore fundamental aspects of long- and short-range electron exchange between electrodes and redox active molecules, such as proteins, is reviewed comprehensively in a chapter by D.H. Waldeck and D.E. Khoshtariya. The authors, who are pioneers in this area, nicely demonstrate that such bioelectrochemical devices with nanoscopically tunable physical properties provide a uniquely powerful system for fundamental electron transfer studies and nanotechnological applications. Studies on protein systems also reveal how the binding motif

vi Preface

of the protein to the electrode can be changed to manipulate its behavior, thus offering many promising opportunities for creating arrays of redox active biomolecules.

A microbial fuel cell (MFC) is a bio-electrochemical transducer that converts microbial biochemical energy directly to electrical energy. In their authoritative chapter, J. Greenman, I.A. Ieropoulos and C. Melhuish overview lucidly the principles of biofilms, biofilm electrodes, conventional fuel cells, and MFCs. Potential applications of both biofilm electrodes and MFCs are suggested, including sensing, wastewater treatment, denitrification, power packs, and robots with full energy autonomy. The symbiotic association between microbial life-forms and mechatronic systems is discussed in detail by the authors, who are internationally renowned experts in this field.

The last three chapters in Volume I deal with surface modification of implants, namely surface biofunctionalization or coating. First, R. Guslitzer-Okner and D. Mandler provide concise survey of different electrochemical processes (electrodeposition, electrophoretic deposition, microarc deposition, electropolymerization, and electrografting) to form different coatings (conducting polymers, non-conducting polymers, sol-gel inorganic-organic polymer materials, oxides, ceramics, bioglass, hydroxyapatite and other calcium phosphates) on different substrates (titanium and its alloys, stainless steels, cobalt-chrome alloys, nitinol, and magnesium alloys). The authors who are highly experienced in this field demonstrate the applicability of these coatings for medical devices such as drug eluting stents and orthopedic implants.

Different electrochemical processes to render metal implants more biofunctional and various electrochemical techniques to characterize the corrosion resistance of implants or the adsorption of biomolecules on the surface are reviewed by T. Hanawa in his authoritative chapter. Electrodeposition of calcium phosphates or polyethylene glycol (PEG), as well as anodizing and micro-arc oxidation processes to obtain TiO₂ nanotube-type oxide film on Ti substrate, or electrochemical treatment to obtain nickel-free oxide layer on nitinol alloys, are described. The effects of different surfaces on phenomena such as cell adhesion, bacterial attachment and calcification are presented.

The last chapter in Volume I, by T. Kokubo and S. Yamaguchi, lucidly summarizes the pioneering work and inventions

Preface vii

of these authors in the field of bone-bonding bioactive metals for orthopedic and dental implants. The metals include titanium, zirconium, niobium, tantalum and their alloys. The main surface modification technique presented in this chapter is chemical, followed by heat treatment, although other techniques such as ion implantation, micro-arc treatment, hydrothermal treatment and sputtering are also described. The bone-bonding ability of metals with modified surfaces is attributable to the formation of apatite on their surface in the body environment, which can be interpreted in terms of the electrostatic interaction of the metal surface with the calcium or phosphate ions in a body fluid. These findings open numerous opportunities for future work.

Volume II begins with a chapter by P.S. Singh, E.D. Goluch, H.A. Heering and S.G. Lemay which provides a lucid overview of the fundamentals and applications of nanoelectrochemistry in biology and medicine. First, some key concepts related to the double layer, mass transport and electrode kinetics and their dependence on the dimension and geometry of the electrode are discussed. Next, various fabrication schemes utilized in making nano-sized electrodes are reviewed, along with the inherent challenges in characterizing them accurately. Then, the "mesoscopic" regime is discussed, with emphasis on what happens when the Debye length becomes comparable to the size of the electrode and the diffusion region. Quantum-dot electrodes and charging and finite-size effects seen in such systems are also described. Then, recent advances in the electrochemistry of freely-diffusing single molecules as well as electrochemical scanning probe techniques used in the investigations of immobilized biomolecules are presented by the authors, who have pioneered several of the developments in this area. Finally, a brief survey of the applications of nanoelectrodes in biosensors and biological systems is provided.

During the last decade, nanowire-based electronic devices emerged as a powerful and universal platform for ultra-sensitive, rapid, direct electrical detection and quantification of biological and chemical species in solution. In their authoritative chapter, M. Kwiat and F. Patolsky describe examples where these novel electrical devices can be used for sensing of proteins, DNA, viruses and cells, down to the ultimate level of a single molecule. Additionally, nanowire-based field-effect sensor devices are discussed as promising building blocks for nanoscale bioelectronic interfaces

viii Preface

with living cells and tissues, since they have the potential to form strongly coupled interfaces with cell membranes. The examples described in this chapter demonstrate nicely the potential of these novel devices to significantly impact disease diagnosis, drug discovery and neurosciences, as well as to serve as powerful new tools for research in many areas of biology and medicine.

The Human Genome Project has altered the mindset and approach in biomedical research and medicine. Currently, a wide selection of DNA microarrays offers researchers a high throughput method for simultaneously evaluating large numbers of genes. It is anticipated that electrochemical detection-based DNA arrays will provide many advantages over radioisotope- or fluorophore-based detection systems. Due to the high spatial resolution of the scanning electrochemical microscope (SECM), this technology has been suggested as a readout method for locally immobilized, micrometer-sized biological recognition elements, including a variety of DNA arrays with different formats and detection modes. In his concise review, K. Nakano explains the underlying electrochemistry facets of SECM and examines how it can facilitate DNA array analysis. Some recent achievements of Nakano and his colleagues in SECM imaging of DNA microdots that respond toward the target DNA through hybridization are presented.

Biological membranes are the most important electrified interfaces in living systems. They consist of a lipid bilayer incorporating integral proteins. In view of the complexity and diversity of the functions performed by the different integral proteins, it has been found convenient to incorporate single integral proteins or smaller lipophilic biomolecules into experimental models of biological membranes (i.e. biomimetic membranes), so as to isolate and investigate their functions. Biomimetic membranes are common in pharmaceuticals, as well as for the investigation of protein-membrane phase stability. interactions. membrane-membrane processes. They are also relevant to the design of membrane-based biosensors and devices, and to analytical platforms for assaying membrane-based processes. The last two chapters in Volume II are dedicated to these systems. In their thorough chapter, R. Guidelli and L. Becucci review the principles and types of biomimetic membranes, the advantages and disadvantages of these systems, their applications, their fabrication Preface

methodologies, and their investigation by electrochemical techniques – mainly electrochemical impedance spectroscopy (EIS). This definitie chapter was written by two authors who are among the leaders leaders in the field of bioelectrochemistry worldwide.

Ion channels represent a class of membrane spanning protein pores that mediate the flux of ions in a variety of cell types. They reside virtually in all the cell membranes in mammals, insects and fungi, and are essential for life, serving as key components in inter- and intracellular communication. The last chapter in Volume II, by E.K. Schmitt and C. Steinem, provides a lucid overview of the potential of pore-suspending membranes for electrical monitoring of ion channel and transporter activities. The authors, who are internationally acclaimed experts in this area, have developed two different methods to prepare pore-suspending membranes, which both exhibit a high long-term stability, while they are accessible from both aqueous sides. The first system, nowadays known as nano black lipid membrane (nano-BLM), allows for ion channel recordings on the single channel level. The second system – pore-suspending membranes obtained from fusing unilamellar vesicles on a functionalized porous alumina substrate – makes it possible to generate membranes with high protein content. The electrochemical analysis of these systems is described thoroughly in this chapter, and is largely based on EIS.

I believe that the two volumes will be of interest to electrochemists, chemists, materials, biomedical and electrochemical engineers, surface scientists, biologists and medical doctors. I hope that they become reference source for scientists, engineers, graduate students, college and university professors, and research professionals working both in academia and industry.

I wish to thank Professor Eliezer Gileadi who was the driving force making me edit these two volumes. I dedicate this project to my wife Billie and our two daughters, Ofri and Shahaf, for their infinite love and support.

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Contents

Chapter 1

MONITORING OF CELLULAR DYNAMICS WITH ELECTROCHEMICAL DETECTION TECHNIQUES

A. Heiskanen and J. Emnéus

I.	Introduction	1
	Monitoring of Cellular Redox Environment	
	Biological Significance of Cellular Redox	
	Environment	4
	(i) Cellular Redox Processes	4
	(ii) Definition of Cellular Redox Environment	7
	(iii) Perturbations in CRE	.11
	(iv) A Functional Definition of CRE	.16
	2. Techniques to Monitor Cellular Redox Environment	.16
	(i) Techniques Utilizing Cell Lysates	
	(ii) Techniques for Live Cells	.17
III.	Monitoring of Exocytosis	.35
	1. Biological Function of Exocytosis	.35
	2. Techniques to Monitor Exocytosis	.40
	(i) Indirect Monitoring Techniques	.41
	(ii) Direct Monitoring Techniques—	
	Electrochemistry	.44
IV.	Monitoring of Cellular Adhesion	.59
	1. Biological Functions of Cellular Adhesion	.59
	(i) In-Vivo Functions	
	(ii) In-Vitro Functions	.61
	2. Techniques to Monitor Cellular Adhesion	.64
	(i) Study of Close Contacts and Focal Adhesions	.64
	(ii) Study of Cellular Morphology	.65

xiv Contents

	(iii) Study of Cellular Adhesion Forces	66
	(iv) Study of Cell-Substrate Interactions	67
V.	Conclusions and Future Perspectives	86
	Acknowledgment	90
	References	90
Cha	upter 2	
	•	
FU	NDAMENTAL STUDIES OF LONG- AND SHORT-RAN	GE
	ELECTRON EXCHANGE MECHANISMS	
	BETWEEN ELECTRODES AND PROTEINS	
	David H. Waldeck and Dimitri E. Khoshtariya	
	,	
I.	Introduction	105
	Theoretical Background	
	General Mechanistic Survey	
	2. The Reorganization Free Energy Parameter	
	3. Temperature, Viscosity, and Pressure Effects	
	4. Electron Transfer for a Freely Diffusing Redox	
	Couple	121
III.	Methodology	
	SAM-modified Electrodes	
	2. Freely Diffusing Species	
	3. Immobilized Species	
IV.	Model Redox-Active species at Au/SAM Junctions	
	1. Overview: The Case of Immobilized Redox Species	
	2. Overview: The Case of Freely Diffusing Redox	
	Species	139
	3. Free $Fe(CN)_6^{3-/4-}$: Impact of SAM Thickness	
	and Solution Viscosity	143
	4. Free $Fe(CN)_6^{3-4}$: Impact of the Variable	_
	Reorganization Energy, Preequilibrium, and	
	Electronic Coupling	147
V	Freely Diffusing Cytochrome C at Au/SAM Junctions	

Contents xv

	1.	The Overview	153
	2.	Impact of the ET Distance (Electronic Coupling)	155
	3.	Impact of Hydrostatic Pressure	
	4.	Links between the Solution (External) vs.	
		Intra-Globular Viscosity	162
VI.	Spe	cifically Immobilized Cytochrome C at Au/SAM	
		ctions	166
	1.	The Overview	
	2.	Pyridine-Terminated SAMs: Impact of the	
		Electron Transfer Distance	171
	3.	Pyridine-Terminated SAMs: Impact of the	
		Solution Viscosity and Heavy Water	178
	4.	Evidence for Dynamic Control rather than	
		Gating at Short Distances	181
	5.	Comparison with Homogeneous Electron Transfer	
		Involving Cytochrome C	185
VII.	Ele	ctrostatically and Covalently Immobilized	
		ochrome C at Au/SAM Junctions	187
	1.	The Overview	
	2.	Results for Cytochrome c Immobilized on Mixed	
		SAMs with Large Chain Length Difference	193
	3.	Kinetic Isotope and Viscosity Effects for Systems	
		with Coulomb and Covalent Binding	197
	4.	Comparison of Different Systems Involving	
		Coulomb, Covalent and Through-Heme	
		Interactions	201
		(i) The Distance for a Transition from	
		Nonadiabatic to Solvent Control	204
		(ii) Effect of SAM Composition on the ET Rate	
		in the Tunneling Regime	205
		(iii) Electron Transfer Mechanism in the Plateau	
		Region	206
	5.	Electron Transfer in the Friction-Controlled	
		Regime	207
VIII.	Αzι	urin at Au/SAM Junctions Immobilized through the	
	Hy	drophobic Patch	209
	1.	The Overview	
	2.	Rate Constants and Reorganization Free Energies	
	3.	Activation Enthalpies from Arrhenius Analysis	

xvi Contents

	4. Activation Volumes from High-Pressure Kinetic	210
IV C	Studiesoncluding Remarks	
	cknowledgementseferences	
K	ererences	222
Chapt	er 3	
MI	CROBIAL FUEL CELLS – SCALABILITY AND THUSE IN ROBOTICS	HEIR
J	ohn Greenman, Ioannis Ieropoulos, and Chris Melhui	sh
I.	Introduction	239
II.	Biofilms	240
III.	Perfusion Biofilms	243
	Misconceptions Regarding Biofilms	
V.	Dynamic Steady State	244
	Biofilm-Electrode Steady State	
VII.	Biofilm Steady States (Quasi Steady State)	247
	Control of the Physicochemical Environment	
	Energy Spilling Mode	
	Biofilm Electrodes	
XI.	Alternative Energy	
	1. Energy from Natural Substrates	
XII.	Conventional Chemical Fuel Cells	
	1. Fuel Cell Principle of Operation	
	2. Types of Fuel Cells	254
	Methane and Carbon Fuel Cells	
XIV.	Microbial Fuel Cells	
	1. MFC Principle of Operation	
	2. The Cathode System	259
	3. MFC Stacks and Scalability	
	4. Internal Resistance5. Cell Reversal in Stacks: An Explanation Why	263
	it is Happening	266
	6. Applications	
	(i) Wastewater Treatment	
	(ii) Denitrification	
	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	

Contents xvii

(iii) Hydrogen	
(iv) Power Packs	269
7. Sensing Using B-E	
8. Processing Using B-E	
9. EcoBots, Symbots, AI and AL	272
10. Artificial Symbiosis	272
11. Robotic Autonomy	273
12. Symbot	279
XV. Discussion	281
References	285
Chapter 4	
ELECTROCHEMICAL COATRIC OF MEDICAL IN	NI ANITO
ELECTROCHEMICAL COATING OF MEDICAL IMI	ZLAN15
Regina Guslitzer-Okner and Daniel Mandler	
Regina Gashizer Okher and Damer Mandrer	
I. Introduction	291
II. The Deposition Method	
1. Electrodeposition (ED)	
2. Electrophoretic Deposition (EPD)	
3. Microarc Deposition (MAD)	
4. Electropolymerization (EP)	
5. Electrografting (EG)	
III. The Substrate	
1. Stainless Steel	
2. Titanium and its Alloys	
3. Nitinol	
4. Magnesium	
5. Cobalt Alloys	
IV. Nature of Deposit	
Polymers (Organic Conducting and	
Non-Conducting)	308
(i) Conducting Polymer Deposits	
(ii) Non-Conducting Polymer Deposits	
2. Sol-Gel (Inorganic-Organic)	
3. Oxides and Ceramics (Inorganic)	
4. Hydroxyapatite and Calcium Phosphate	

xviii Contents

5. Metals	328
V. Conclusions	330
References	
Chapter 5	
ELECTROCHEMICAL TECHNIQUES TO OBTAI	N T
ELECTROCHEMICAL TECHNIQUES TO OBTAI	IN
BIOFUNCTIONAL MATERIALS	
Takao Hanawa	
I Internation	2.42
I. Introduction II. Overview of Current Electrochemical Treatments	
III. Electrodeposition of PEG	
Electrodeposition of FEG Electrodeposition Process and its Effects	
Evaluation of the Thickness of the Immobilized	347
Layer with Ellipsometry	250
IV. Electrodeposition of PEG Twitter Ions to Accelerate	330
Cell Adhesion	
The Isoelectric Points of PRG Twitter Ions	332
According to pH	352
The Effect of RGD Peptide Immobilized through	
PEG on Calcification by MC3T3-E1	
V. Nickel-Free Surface Oxide Film on Ti-Ni Alloy	
VI. Cathodic Polarization for Characterization of Metal	
Surfaces	358
Changes of Surface Composition	
(i) Titanium	
(ii) Stainless Steel	
(iii) Cobalt-Chromium-Molybdenum Alloy	
(iv) Zirconium	
2. Difference between Calcium Phosphate Formation	
on Titanium and Zirconium	
(i) Cathodic Polarization	
(ii) Characteristics of the Surface Oxide Film	370

Contents	xix
contents	244.1

VII.	Electrochemical Measurements	370
VIII.	Quartz Crystal Microbalance (QCM)	372
	References	
Chapt	er 6	
-		
	BIOACTIVE METALS PREPARED BY SURFACE	
N	IODIFICATION: PREPARATION AND PROPERTIE	S
	Tadashi Kokubo and Seiji Yamaguchi	
	, , ,	
I.	Introduction	377
II.	Requirements for Bioactive Materials	378
	Bioactive Ti Metal and its Alloys	
	1. Surface Modification with Sodium Titanate	
	2. Surface Modification with Calcium Titanate	391
	3. Surface Modification with Titanium Oxide	400
	4. Principles for Preparing Bioactive Ti Metal and its	
	Alloys by Surface Modification	411
IV.	Bioactive Zr Metal	
	Bioactive Nb Metal	
VI.	Bioactive Ta Metal	413
VIII.	Summary	414
	References	
	Index	

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Modern Aspects of Electrochemistry

Topics in Number 50 include:

- Investigation of alloy cathode Electrocatalysts
- A model Hamiltonian that incorporates the solvent effect to gas-phase density functional theory (DFT) calculations
- DFT-based theoretical analysis of ORR mechanisms
- Structure of the polymer electrolyte membranes (PEM)
- ORR investigated through a DFT-Green function analysis of small clusters
- Electrocatalytic oxidation and hydrogenation of chemisorbed aromatic compounds on palladium
 Electrodes
- New models that connect the continuum descriptions with atomistic Monte Carlo simulations
- ORR reaction in acid revisited through DFT studies that address the complexity of Pt-based alloys in electrocatalytic processes
- Use of surface science methods and electrochemical techniques to elucidate reaction mechanisms in electrocatalytic processes
- In-situ synchrotron spectroscopy to analyze electrocatalysts dispersed on nanomaterials

Topics in Number 51 include:

- Temperature effects on platinum single-crystal and aqueous solution interphases
- Surface thermodynamics of the metal and solution interface
- XAS investigations of PEM fuel cells
- Palladium-Based electrocatalysts required for alcohol oxidation in direct alcohol fuel cells
- Structure and Reactivity of transition metal chalcogenides used for molecular oxygen reduction reactions
- Proton conductivity and electrocatalysis in high temperature PEM fuel cells