Bioinorganic Electrochemistry

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Springer

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 978-1-4020-6499-9 (HB)
ISBN 978-1-4020-6500-2 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

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Preface

Interfacial electrochemistry of redox metalloproteins and DNA-based molecules is presently moving towards new levels of structural and functional resolution. Underlying fundamentals of electron and proton transfer are increasingly well understood although also with new challenges relating to the composite interfacial solid-electrolyte environment. The new inorganic bioelectrochemistry draws further from comprehensive studies of the interfacial environments for retaining biological charge transfer function of these highly sensitive macromolecular systems. Other biotechnology has been the use of mutant proteins, DNA-base variability and *de novo* synthetic metalloproteins.

Physical electrochemistry underwent a remarkable evolution from the 1970's, almost to be likened by a renaissance and prompted by close interaction between electrochemistry and surface physics. The introduction of single-crystal atomically planar electrode surfaces was a major breakthrough and laid the foundation for other new technology such as spectroscopic techniques and statistical mechanical and electronic structure theories. Only slightly later scanning tunneling (STM) and atomic force microscopy (AFM) signalled a lift of interfacial electrochemistry to unprecedented structural resolution. Atomic resolution of pure metal and semiconductor electrode surfaces and at least sub-molecular resolution of electrochemical adsorbates could be achieved, opening new worlds of microscopic structures and processes.

Similar boundary-traversing efforts are now visible in interfacial electrochemistry of proteins and DNA-based molecules. This has led to

improved voltammetric sensitivity and structural mapping of the bioelectrochemical solid-liquid interface to single-molecule resolution. It is in fact remarkable that molecules as large and fragile as redox metalloproteins adsorbed on electrode surfaces can be mapped in their functional state by a subtle physical phenomenon, the quantum mechanical tunneling effect. These openings have offered new theoretical challenges for electron tunneling through biological macromolecules, the role of the metal centres, and the finite-size stochastic nature of the systems. Combination of protein and DNA biotechnology with electrochemistry has come to offer other perspectives in bioelectrochemical signal transfer between target molecules and external electrochemical circuitry based on strategic surface preparation and functional linker molecules.

The chapters in this volume offer overviews of electronic properties, electron transfer and electron-proton coupled charge transfer of biological molecules and macromolecules both in the natural aqueous solution environment and on metallic electrode surfaces, where the electrochemical potential controls biomolecular function. Redox metalloproteins and DNA-based molecules are primary targets, but amino acid and nucleobase building blocks are also addressed. Novel environments where proteins and DNA-based molecules are inserted in metallic nanoparticle hybrids or *in situ* STM configurations are other focus areas.

The chapters by Winkler *et al*. and by Wikström overview electron and electron-proton coupled charge transfer of both small electron transfer metalloproteins and large metalloenzyme complexes such as cyt *c* oxidase. A key point is the mechanistic detail now available. Percolation of electrons through the protein structure and proton hopping through conduction channels in the enzyme structures, triggered by electron transfer are important issues. Understanding of these patterns is a prerequisite for protein and enzyme voltammetry and hybrid systems for working enzyme-devices. Such perspectives are addressed by Willner and Willner, and by Butt and Armstrong. It is notable that large and fragile, sometimes multi-component enzymes can be controlled and retain close to full enzyme function at the electrochemical interface to the extent where molecular mechanisms of enzyme electrocatalysis can be mapped. This holds perspectives for multifarious technology for example in metalloenzyme biosensor function. Functional units which respond to optical, magnetic, and other signals can further be inserted between the electrode and the enzymes and biological redox chains constructed.

The chapter by Hill and Kelley addresses the interfacial electronic conductivity of DNA-based molecules controlled by the electrochemical potential. Binding of redox probes is a probe for electronic communication between the probe and the electrode through the DNA-molecular frame and therefore of the tunneling conductivity of the latter. This remains an intriguing issue as the redox-based electronic energies of the nucleobases are strongly off-resonance with the electrode Fermi energy and the redox level of the probe molecule.

Single-crystal, atomically planar electrode surfaces have paved the way for the scanning probe microscopies, STM and AFM in bioelectrochemistry. The chapter by Nichols *et al*. illuminates this powerful technology which has increased the structural resolution of the (bio)electrochemical electrode surfaces to sub-molecular levels. High-resolution images have been achieved for the biological building blocks, i.e. DNA nucleobases and amino acids, both of which form highly ordered monolayers on Au(111)- and Pt(111) - electrode surfaces. Dynamic surface phenomena such as adlayer phase transitions can also be followed. The image detail of individual molecules and patterns in their lateral organization holds clearly perspectives for understanding the interaction of biological liquids with solid surfaces.

The use of STM/AFM to biological macromolecules is discussed further in the chapters by Kuznetsov and Ulstrup, and by Zhang *et al*. Single-molecule resolution has been achieved for both redox metalloproteins and DNA-based molecules under conditions where the molecules are active in electron transfer or enzyme function. Not only structural mapping but given adequate theoretical support, electron transfer and redox enzyme function can be addressed at the single-molecule level. The Os-complexes and the redox metalloprotein, *P aeruginosa* azurin discussed in chapter 8 illuminate these perspectives which extend towards ultra-sensitive biological sensors and other "device" function. STM and in *situ* STM are theoretically demanding because the electrical current recorded does not translate directly into molecular topography. Long-range off-resonance conductivity is broadly understood in terms of electron exchange and energy gaps of appropriate atomic or molecular orbitals with exponential distance dependence of the tunneling current expected. This is sometimes observed but weak current attenuation emerges in other cases such as for single- and double-stranded oligonucleotides. This issue presently appears unsettled.

Electronic conductivity of (bio)molecules with low-lying redox states show a quite different pattern, namely two- (or multi-)step hopping through the redox state(s) induced by environmental configurational fluctuations.

Theoretical notions rest on electrochemical electron transfer but the novel environments have also disclosed new electron transfer phenomena. Switching or negative differential resistance, quite different from electrochemical electron transfer at semi-infinite electrode surfaces is immediately conspicuous. Coherent, multi-electron transfer in a single *in situ* STM event is another non-traditional electron transfer phenomenon.

(Bio)molecular electronics, enzyme electrochemistry, oligo-nucleotide organization, and high-resolution biological screening are exciting parts of new bioelectrochemistry. Networks of hybrid biomolecular structures are other novel targets. In a biotechnological perspective, fundamental bioelectrochemical innovation remains, however, essential. The objective of this volume is to illuminate these exciting new stages of bioinorganic electrochemistry.

Copenhagen and Lyngby, June 2007

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http://www.springer.com/978-1-4020-6499-9

Bioinorganic Electrochemistry
Hammerich, O.; Ulstrup, J. (Eds.)
2008, XIV, 310 p., Hardcover
ISBN: 978-1-4020-6499-9