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Chem. Rev., **2008**, 108 (7), 2111-2112 • DOI: 10.1021/cr8004026 • Publication Date (Web): 11 July 2008

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Introduction: Molecular and Biomolecular Electrochemistry



Jean-Michel Savéant received his education in the Ecole Normale Supérieure in Paris, where he became the Vice-Director of the Chemistry Department before moving to the University Denis Diderot (Paris 7) as a Professor in 1971. He is, since 1985, Directeur de Recherche au Centre National de la Recherche Scientifique in the same university. In 1988–1989 he was a distinguished Fairchild Scholar at the California Institute of Technology. His current research interests involve all aspects of molecular and biomolecular electrochemistry as well as mechanisms and reactivity in electron transfer chemistry and biochemistry. Among many distinctions, Jean-Michel Savéant received the Faraday Medal of the Royal Chemical Society, the Olin Palladium Medal of the Electrochemical Society, la Medaglia Luigi Galvani della Società Chimica Italiana and the Manuel Baizer Award of the Electrochemical Society. Jean-Michel Savéant is a member of the French Academy of Sciences and foreign associate of the National Academy of Sciences of the United States of America.

Maybe the most straightforward definition of “Molecular Electrochemistry” is through a double motto: “molecules for electrochemistry and electrochemistry for molecules”. As opposed to the equally important segment of electrochemistry that investigates or uses surface states directly involving the electrode material, molecular electrochemistry deals with the transformation of molecules triggered by electron transfer from or to an electrode and/or by the use of molecules dispersed in the solution or attached to the electrode surface to accelerate and optimize an electrochemical reaction. In such cases, the nature of the electrode material is expected to play a minor role, with the electrode serving essentially as an “innocent” electron reservoir or sink. Under these conditions, there is a strong link between molecular electrochemistry and other areas of electron transfer chemistry where the electron comes from or goes to a molecular reactant introduced in the solution as such or photogenerated from a stable ground state. The advantages of molecular electrochemistry in this respect are that imposing the electrode potential is an easy way of adjusting the driving

force of the reaction and that the current flowing through the electrode is a convenient measure of the reaction kinetics.

As in many other domains of physical chemistry, the motivations of the contemporary studies in molecular electrochemistry are increasingly directed toward natural systems in order to understand, imitate, or exploit them. This tendency is reflected in the title of this thematic issue, which was expanded to “Molecular and Biomolecular Electrochemistry”, even if it may appear redundant since biomolecules are molecules. Over the nineteen contributions to the issue, eight are indeed dealing directly with natural species or reactions and one is strongly inspired by the understanding and mimicking of biological reactions.

Another major tendency in recent developments of molecular and biomolecular electrochemistry is downsizing, en route to nanoelectrochemistry or even to molecular electronics.

Even though the perspectives and motivations of molecular and biomolecular electrochemistry have evolved over the last twenty years, the necessity of addressing fundamental problems of electron transfer chemistry through electrochemistry remains. This is the case with the question of one-electron vs two-electron transfer, still of high current interest, which is treated in the contribution of Dennis H. Evans, One-Electron and Two-Electron Transfers in Electrochemistry and Homogeneous Solution Reactions. Another fundamental question concerns the association between electron transfer and proton transfer. This rather old problem is currently receiving much renewed attention in connection with the importance of such processes in biological reactions. Cyrille Costentin addresses the question under the electrochemical angle in his contribution Electrochemical Approach to the Mechanistic Study of Proton-Coupled Electron Transfer. How breaking and formation of bonds involving heavy atoms can be triggered by electron transfer, particularly electrochemical electron transfer, is a key question that, together with proton–electron transfer coupling, underlies the chemical transformations produced by means of electrochemistry and, more generally, by injection or removal of an electron. This topic is reviewed in Abdelaziz Houmam’s article Electron Transfer Initiated Reactions: Bond Formation and Bond Dissociation. Electrochemistry without solvent is another fundamental matter of timely interest, which may receive interesting clean-chemistry applications in the near future. It is scrutinized by Philippe Hapiot and Corinne Lagrost in their article Electrochemical Reactivity in Room-Temperature Ionic Liquids.

Among the motivation and applications of molecular electrochemistry, electrochemical organic synthesis is a domain of continuously renewed interest. Jun-ichi Yoshida,

Kazuhide Kataoka, Roberto Horcajada, and Aiichiro Nagaki review its current developments in their contribution *Modern Strategies in Electroorganic Synthesis*. One particularly important tool of organic synthesis is organometallic catalysis. The role of electrochemistry in this domain is highlighted by Anny Jutand in her review *Contribution of Electrochemistry to Organometallic Catalysis*.

Still dealing with catalysis, but rather directed to the activation of small molecules, Jean-Michel Savéant's contribution *Molecular Catalysis of Electrochemical Reactions. Mechanistic Aspects* emphasizes the importance of biological inspiration, in particular that provided by enzymes, thus making a transition to the contribution of electrochemistry to the understanding of how redox enzymes work, as examined in Christophe Léger and Patrick Bertrand's review *Direct Electrochemistry of Redox Enzymes as a Tool for Mechanistic Studies*. Proceeding along the same lines, direct use of enzymes or the inspiration they may provide in the design of artificial catalytic systems is extensively reviewed in James A. Cracknell, Kylie A. Vincent, and Fraser A. Armstrong's article *Enzymes as Working or Inspirational Electrocatalysts for Fuel Cells and Electrolysis*.

Getting to the heart of biomolecular electrochemistry, the contribution of George S. Wilson and Michael A. Johnson *In-Vivo Electrochemistry: What Can We Learn about Living Systems?* provides a wide overview of enzyme electrode biosensors and of direct electrochemistry of endogenous electroactive species with strong emphasis on the problems to be faced under *in vivo* conditions. Continuing with enzyme electrodes, application to a particularly important health problem is discussed in depth in Adam Heller and Ben Feldman's contribution *Electrochemical Glucose Sensors and Their Applications in Diabetes Management*. Application of another phenomenon, electrochemically generated chemiluminescence, to the detection and quantification of biological analytes is a useful complement to direct electrochemical techniques. Recent developments in this area are examined by Wujian Miao in his contribution *Electrogenerated Chemiluminescence and Its Biorelated Applications*, which also provides indispensable information on principles, mechanisms, and available instrumentation.

Detection and quantification of biological analytes also form the basis of two other contributions. One, by Donita L. Robinson, Andre Hermans, Andrew T. Seipel, and R. Mark Wightman, describes how daunting analytical challenges in the detection of neurotransmitters are overcome by electrochemical means so as to permit *Monitoring Rapid Chemical Communication in the Brain*. How similarly daunting challenges can be dealt with successfully in studies of single cell metabolism is reviewed in an article by Christian Amatore, Stéphane Arbault, Manon Guille, and Frédéric Lemaître: *Electrochemical Monitoring of Single Cell Secretion: Vesicular Exocytosis and Oxidative Stress*. In this case, too, such achievements of *in vivo* electrochemistry would have seemed unattainable just a few years ago.

Electron transfer through DNA has been the object of very active and somewhat controversial attention in recent years. In their contribution *Electron Transfer in DNA and in DNA-Related Biological Processes. Electrochemical Insights*, Fabien Boussicault and Marc Robert review the state of

knowledge in this field with attention to related questions, such as repair of DNA lesions by photolyases, with emphasis throughout on the contribution of electrochemistry.

All electrochemical approaches described in the above and following contributions require the choice of an appropriate electrode material that does not interfere too strongly in the processes of interest and that leads to reproducible results. The limitations of mercury in these two respects make one yearn for the halcyon days of the reign of the easily reproducible mercury electrode. Gold and platinum allow more incursions into the oxidation domain, but the formation of surface oxides at relatively low potentials makes these noble metals less noble than one would have imagined. Carbon thus appears as a valuable alternative, even if not devoid of reproducibility problems. Richard L. McCreery reviews the use of various brands of carbon, including diamond, in his article *Advanced Carbon Electrode Materials for Molecular Electrochemistry*, which also addresses the important and timely topic of the derivatization of carbon electrode surfaces, particularly by means of the popular diazonium technique.

In many of the above contributions, getting to increasingly smaller dimensions of electrodes and cell volumes has emerged as a major means of achieving important goals. We thus arrive progressively at the notion of "Nanoelectrochemistry", in keeping with the general developments of nanosciences. In his contribution *Nanoelectrochemistry: Metal Nanoparticles, Nanoelectrodes, and Nanopores*, Royce W. Murray gathers the main aspects of these recent developments, addressing not only the use of small electrodes but also the potential and problems of small volumes. With regard to small electrodes, an article devoted to the scanning electrochemical microscopy (SECM) technique is obviously missing in the present issue. This is because it would have duplicated a review by Shigeru Amemiya, Allen J. Bard, Fu-Ren F. Fan, Michael V. Mirkin, and Patrick R. Unwin, which is to appear soon in *Annual Review of Analytical Chemistry*.

Downsizing further, we come to molecular dimensions and thus to the relationships between Electrochemistry and Molecular Electronics, a booming field not devoid of artifact risks. This is the subject of the two last, but not least, reviews of this thematic issue: *Electron Transfer through Molecules and Assemblies at Electrode Surfaces*, by Burak Ulgut and Héctor D. Abruña, and *Single-Molecule Electron Transfer in Electrochemical Environments*, by Jingdong Zhang, Alexander M. Kuznetsov, Igor G. Medvedev, Qijin Chi, Tim Albrecht, Palle S. Jensen, and Jens Ulstrup.

In composing this thematic issue, we did not attempt to provide a completely exhaustive coverage of all aspects of molecular and biomolecular electrochemistry but rather to highlight particularly illustrative examples of its recent developments. I am convinced that the reader will be struck, as I am, by the amazing diversity of the domains reached by a discipline whose concepts and procedures remain unified albeit continuously enriched.

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